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ENVIRONMENTAL INNOVATIONS IN NITROPHOSPHATE TECHNOLOGY

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Gujarat Narmada Valley Fertilizers Co Ltd (GNFC) est la société leader du secteur commun multiproduit avec des unités d'ammoniac et d'urée dans la phase 1 de son projet au début des années 1980. Une partie du projet d'expansion portait sur la construction d'un atelier de nitrophosphate devenu opérationnel en 1989-90. Parmi les nombreuses technologies disponibles pour la production de NPK, la technologie, économique et favorable à l'environnement, de production d'ammonitrate de calcium (CAN) basée sur la granulation en pétrin et de nitrophosphate d'ammonium (ANP) basée sur le procédé ODDA, ont été choisies. Ces unités sont fournies par Krupp-Uhde, Allemagne, et BASF, Allemagne. Cet exposé décrit le soin spécial apporté dans l'engineering pour maintenir les flux d'azote ammoniacal et nitrique et d'effluent contenant P_2O_5 et les courants de récupération séparément pour chaque section avec un système de contrôle adéquat de l'environnement.

Les innovations ont été apportées à différentes sections en recyclant les effluents, en contrôlant les paramètres strictes du procédé et l'emploi de différents phosphates bruts. L'effluent généré lors de la fabrication des ANP est recyclé selon un plan modifié en même temps que la digestion du phosphate. GNFC a incorporé un cyclone très efficace dans l'unité de CAN. Dans l'unité de séchage de la chaux, un multi-cyclone a été installé et, ultérieurement, un filtre à été amélioré en installant des sacs PTFE agrandis. La méthode de détection innovante des fuites avec poudre fluorescente a été déployée. Avec cela les émissions de matières solides en particules ont diminué bien en dessous de 100mg/Nm^3. Comme stratégie d'approche d'environnement plus propre GNFC érige un système de lavage humide en employant l'effluent généré dans le procédé pour les unités d'ANP et de CAN. Les trop pleins du laveur seront employés dans le procédé après concentration. Sur l'exploitation des déchets solides, des standards très élevés sont maintenus et des améliorations sont obtenues avec des systèmes spéciaux comme les stockages protégés etc. Le système de dépoussiérage est installé pour chaque équipement de sorte que l'environnement dans et autour des appareils demeure plus propres.

En déployant des méthodes innovantes de recyclage, réemploi de l'effluent et évaporation pour retraitement, GNFC se rapproche de l'objectif d'un environnement plus propre.

ABSTRACT:

Gujarat Narmada Valley Fertilizers Co. Ltd. (GNFC), a India's leading multi-product joint-sector company, put up a single stream ammonia and urea plants in phase one of its project in the early 1980's. As a part of the expansion project, the nitrophosphate production facility was put up and it became operational in 1989-90. Out of many technologies available for NPK production facility, economical and eco-friendly technology of producing calcium ammonium nitrate based on pug-mill granulation and ammonium nitrophosphate based on ODDA process

were selected. These plants were supplied by Krupp Uhde, Germany and BASF, Germany. This paper describes the specific care taken in engineering to keep ammonical and nitrate nitrogen and P2O5-bearing effluents and recovery streams separately for each section with adequate environment control system.

The innovations were done in various sections by recycling effluents, controlling stringent process parameters and use of different rock phosphates. The effluent generated during ANP manufacturing is being recycled with modified scheme along with rock digestion. GNFC has put up highly efficient cyclone in the CAN plant. In the lime drying unit, multi-cyclone was installed and subsequently the bag filter was upgraded by installing expanded PTFE bags. Innovative leak detection method with fluorescent powder was deployed. With this the solid particulate matter emissions have come down well below 100 mg/Nm^3. As a strategy to approach cleaner environment, GNFC is putting up wet scrubbing system by use of effluent generated in the process for ANP and CAN plants. The bleeds from the scrubbers shall be used in the process after concentration. On the solid waste management, very high standards are being maintained and upgradations are done with special facilities like protected storages, etc. De-dusting system is being installed at each of the equipment so that environment in and around the equipment also remains cleaner.

By deploying innovative methods for recycle, reuse of effluent and evaporating for reprocessing GNFC is approaching its goal of cleaner environment.

INTRODUCTION:

Gujarat Narmada Valley Fertilizers Co. Ltd. (GNFC) is one of the world's largest single stream fuel oil based ammonia and urea complex located at Bharuch, Gujarat State. GNFC started its operation with 1350 MTPD ammonia and 1800 MTPD urea plants in January 1982. After stabilizing the operations of both the plants at more than their name plate capacity, the company expanded its operations to phosphatic fertilizers (ANP - CAN) and industrial chemicals like WNA, CNA, methyl formate, formic acid, acetic acid, methanol, aniline and TDI. Along with above chemical plants, the Company has also successfully diversified into electronic field for productions of PCB, RAX, PAX. Recently the Company has entered into the new field of information technology and is likely to expand further.

NITROPHOSPHATE COMPLEX

The Nitrophosphate Complex of GNFC includes an integrated ammonium nitrophosphate and calcium ammonium nitrate fertilizers plants, each having a capacity of 475 MTPD. A 630 MTPD subsequently revamped to 750 MTPD weak nitric acid plant (WNA) supplies nitric acid for captive consumption and is also used to operate two concentrated nitric acid (CNA) plants having capacity of 100 MTPD.

The ANP plant operates on the basic ODDA Process with the process know-how supplied by BASF, Germany and basic engineering done by Krupp Uhde, Germany.

The main steps of ANP process are as under :

a) Rock phosphate storage and handling.

b) Dissolution of rock phosphate with nitric acid.
c) Crystallization of the dissolving solution and separation of calcium nitrate crystals from nitrophosphate acid.
d) Ammoniation i.e. neutralization of NP acid (N : P ratio fixation).
e) Granulation of the slurry and conditioning of the product.
f) Conversion of CN crystals to ammonium nitrate and lime.
g) Concentration of ammonium nitrate.

Calcium carbonate and ammonium nitrate are the byproducts of this process. A part of ammonium nitrate and calcium carbonate are used for production of calcium ammonium nitrate fertilizer. The rest of calcium carbonate is disposed off, while remaining ammonium nitrate solution is used in ANP plant for N : P_2O_5 ratio correction. A small quantity of sand separated from rock phosphate is recycled as filler while the main stream of the sand is added in granulation section.

The schematic block diagram of overall ANP and CAN process plants highlighting all the sections is shown in Figure I and the neutralization, granulation and conditioning sections are shown in Figure II and IIa. Table I indicates the rise in production level since commissioning.

TABLE - I

PRODUCTION AND CAPACITY UTILIZATION OF ANP & CAN PLANTS

YEAR	ANP		CAN	
	PROD (in MT)	*CU (%)	PROD (in MT)	CU (%)
1991-92	123,654	87	62,526	44
1992-93	141,491	99	93,807	66
1993-94	133,873	94	160,547	113
1994-95	149,304	105	143,678	101
1995-96	150,522	106	156,160	110
1996-97	137,282	96	144,060	101
1007-98	155,704	109	170,738	120
1998-99	150,812	106	152,689	107
1999-00	155,899	109	128,143	90

*CU - CAPACITY UTILIZATION

AMMONIUM NITROPHOSPHATE PLANT
MAJOR LIQUID EFFLUENTS

Following table indicates the major liquid effluent streams from ANP/CAN plants.

TABLE -II

LIQUID STREAMS

Stream	Unit	Sand	Condensate	NOx Gas	Discontinuous waste
Parameter ↓					
Design flow per day	m^3	288.0	136	595	240
PH	---	5.0	4	5	4
NO_3(N)	**mg/lit**	1594	685	1340	435
NH_4(N)	**mg/lit**	1231	701	---	365
P_2O_5	"	804	---	16	217
CaO	"	1231	---	27	328
SiO_2	"	0.54	119	1.1	41
F	"	72	225	54	87

LIQUID EFFLUENT RECYCLE/REDUCTION:

In early stages of plant operation, after commissioning, a lot of effluent was generated due to unstable operation with many start-ups and shutdowns. But after stabilization of plants with a view to reduce the liquid effluent generation, various innovative ideas and new schemes have been implemented. This has given the wonderful result with drastic reduction in volumetric flow rate with same loading of nutrients, making the operation efficient with maximum nutrient recovery from liquid effluents. Following list describes in brief the various major schemes implemented in past 4-5 years of operation, which have not only saved liquid effluents but also has generated lot of saving in treatment cost of liquid effluents.

A) **REDUCTION IN DISCONTINUOUS EFFLUENT STREAM**:

Due to stringent water balance across the digestion/CN filtration step in ODDA process, it was quite difficult to recycle any acidic effluent to the process. The attempts made to recycle these effluents were not successful as the NP acid quality was disturbed and thereby causing load reduction and production losses. Following two steps were taken to create favourable conditions of recycling concentrated effluent.

1) **Wash acid mixing with NP acid:**
By mixing a part of wash acid, generated in calcium nitrate filtration section to NP acid, the recycled water to the digestor was reduced, in turn this has created opportunity to recycle more water through the concentrated effluent streams.

2) **Increase in nitric acid concentration:**
The concentration of nitric acid produced in WNA plant was increased from 60 to 62%. This increase in concentration of acid fed to digestors created the scope of putting more water through liquid effluent streams, without affecting the quality of dissolving solution.

In view of above, a modification was implemented for monitoring continuity of recycling of effluent. The salient features of this scheme are as follows:

i) Collection of effluents from underground effluent pits to intermediate tank (~ 5 m^3 volume).

ii) Recycle of effluent from tank to digestor with a flow control valve in cascade with main nitric acid flow to tank in case of load variation.

iii) Provision of recycle of part of sand washing in case of shortage of discontinuous pit effluent.

iv) Recently one more tank of 100 m^3 has been erected and commissioned for storing the large volume of discontinuous rich effluent which gets generated during shutdown/washing/overflowing of tanks.

With implementation of above schemes, we have been successful not only in maintaining the continuity of effluent recycle but also in recovering part of sand wash effluent too. The total discontinuous effluent now being generated is around 30 m^3/day against design value of 240 m^3/day. (The schematic sketch for above modification is given in Figure III).

B) **REDUCTION IN NOx WATER EFFLUENT:**

The NOx gases which are continuously generated from various tanks of digestion and CN filtration sections are scrubbed in 32C001 & 2C002 absorption towers. The fresh water is added to 32C002 and part of NOx water is circulated in 32C002 & 32C001. The NOx bearing effluent is then continuously transferred to effluent treatment plant. By modification, the part of the effluent is diverted to 32D013 (make up tank) and there is a reduction in fresh make up of equivalent quantity. By this modification, the quantity of NOx effluent is reduced by 100 m^3/day. There also reduction in fresh water consumption. (The schematic sketch for above scheme is shown in Figure IV).

C) **RECOVERY OF NUTRIENTS FROM SAND WASHINGS /EFFLUENT**:

The nutrient content (P_2O_5 & NO_3-N) in sand effluent discharged to effluent treatment plant remained very high as sand was washed on inert filter by nitric acid only.

To recover these nutrients, a scheme was recently implemented which is described below:
From 2nd vacuum separator of inert filter, the wash is taken to the effluent recycle tank (79 T002) and from the same tank again the wash is given in inert filter to wash the sand. By this washing, the P_2O_5 and NO_3-N adhered to sand is washed.

The part of the liquid from this circulation loop is taken to digestor in controlled way for recovery and adjusting the water balance.

The comparative data of nutrient in sand effluent, before and after implementing the modification is furnished in following table.

	Unit	NH_4-N	NO_3-N	F	P_2O_5	Flow/m^3 day
Design	mg/m^3	---	1542	2	21	288
For period April to July	mg/m^3	24	5728	485	7717	~ 30
Aug. 99 to March 2000	mg/m^3	11	825	55	766	~ 30

From the above, it reveals that there is drastic reduction in nutrient level (one tenth) which has given a considerable saving in terms of nutrient recovery and cost of sand wash effluent treatment.

(The schematic sketch for above scheme is shown in Figure V).

POLLUTION CONTROL MEASURES IMPLEMENTED FOR GRANULATION DRYING AND CONDITIONING SECTION:

The emission level of particulate matter through the final stack 36V001 remained very high during disturbance in granulation for various reasons, generating more dusty products which choke cyclones very frequently and the emission level exceeding by 2 - 5 fold against the prescribed limit. Following innovative ideas/schemes have been implemented in period of past couple of years which has brought wonderful results of stack emission, for which comparative data are furnished below for past five years of operation.

STACK EMISSION DATA

Year	36V001 (Particulate matter)		35K001 (Ammonia Gas)	
	Abnormality	Total samples	Abnormality	Total samples
1995-96	105	236	0	95
1996-97	53	127	0	67

1997-98	32	96	0	39
1998-99	24	119	21	57
1999-00	2	145	6	69
LIMIT = 150 mg/NM^3			LIMIT = 175 mg/NM^3	

To improve upon the particulate matter emission, following major schemes were implemented:

A) Three of the screw conveyors provided below the cyclones system were removed and the discharge ducts were joined. This was done due to frequent mechanical failure of screws due to dust load and lump formation which was jamming the screws and subsequent failures. This in turn caused choking of cyclone system (one stream) and very high PM/dust emission to atmosphere. After this modification, the stack results have improved drastically since past two years of operation and the emission has remained below the prescribed limit of pollution control board.

B) **MODIFICATIONS IN CYCLONE SYSTEM**:

i) The chains were provided in all the 9 cyclones to avoid its choking due to whirling motion of the chains which keeps the inside conical and duct area clean.

ii) The critical relative humidity (CRH) of ANP product is 55%. Hence the ingress of any humid air through false air sucking from cyclone cover/duct cover led to leaching out of ANP dust and thereby choking the cyclone outlet ducts/flaps. These covers were modified with better sealing arrangement thereby solving the local choking of material to a great extent.

iii) The pendulum flaps are provided below the 3 cyclone battery to discharge the dust and recycle to granulator. This flap also acts as sealing medium to avoid false air sucking to cyclone due to negative draft available in cyclones. Due to rough inside surface of the flaps, the ANP dust was jammed inside the flap, choking the flap and in turn cyclones was very high. These three flaps were provided with teflon lining and thereafter the choking tendency of these flaps have reduced drastically and thereby improving cyclone system performance a great deal.

iv) On experimental basis, certain carbon steel ducts were replaced by neoprene rubber hoses in the cyclone outlet ducts. The results were encouraging as the rubber ducts have following advantages over carbon steel/stainless steel ducts.

a) Flexibility, hence vibrations level transmission is high which will restrict choking tendency.

b) During choking of duct, the de-choking is easy as simple hammering will discharge the material without deformation.

c) Rubber ducts are bad conductor of heat and hence atmospheric effect during humid / winter season will be very less which will avoid choking tendency due to local cooling of material i.e. ANP dust.

The results were encouraging for the past six months and hence in last turn around of April 2000, all the ducts of cyclone system were replaced with neoprene rubber ducts and the system is kept under observations. (The schematic sketch for all above modifications is shown in figure VI).

CALCIUM AMMONIUM NITRATE PLANT:

ENVIRONMENTAL BREAKTHROUGH IN EMPLOYING BAG FILTER TECHNOLOGY

GNFC faced the problem of higher stack emissions connected with the lime drying unit bag filter. A significant breakthrough was achieved with the help of innovative techniques employed with respect to bringing down the emissions below 100 mg/Nm^3 most of the times and increasing continuity of operations, minimizing number of interruptions and reducing maintenance drastically.

This breakthrough was achieved by systematic approach and efforts.

Brief description;

Firstly, efforts were put to identify the problems and define them. The major problems were :

1) Higher emissions from bag filter.
2) Frequent choking of bag filter.
3) Load limitation in flash dryer as choking bag filter did not permit required air flow.
4) Interrupted operations of flash dryer and CAN plant.

Secondly, multi-cyclones were installed upstream of bag filter to reduce its load and enhance performance. The possibility of eliminating bag filter if multi-cyclones function well was explored. No significant advantages could be accrued and bag filter emission, operational problems never eased.
Thirdly, detailed performance evaluation of each separator was carried out. It was observed that main cyclones were performing well with efficiency 96-98%, but efficiency of multi-cyclones remained poor and varying between 36.3% to 80%.

The reason for the same result was identified : a significant portion of lime was below 6 micron size. Therefore it became clear that cyclone/multi-cyclone alone cannot separate lime from air stream with high efficiency and performance of bag filter needs to be upgraded so that it can remain healthy even with sub-micron particles. It was observed that with conventional Nomex bags, bag filter was quickly exhausted and revival was not satisfactory due to impregnation of bag openings with fine lime particles permanently. Higher emissions were due to leakages from gaskets (3 layer) of bag collar because of gaskets becoming brittle/stiffened on heating, tearing of bags on account of piercing by broken wires of cages, and buckling of cages.

Finally, efforts were made to get expert services from various vendors. The expert services of BHA Group International were engaged for eliminating bag filter problems. After inspection by BHA, following measures were implemented:

i) Installing, expanded PTFE membrane laminated bags which is latest concept and break through in filtration technology. This concept is called surface filtration technique. This high tech material does away with the requirements of precoat, has efficiency of 99.992% with particles size of 80-84% smaller than 0.578 microns, offers lower pressure drop hence more overall efficiency and capacity and bags never clog permanently even with sticky materials.

ii) Installing good quality cages in terms of high strength, absence of sharp edges points (to prevent bag piercing) good quality welding (on computerize welding machines).

iii) Development and employment of bag/ cage, of leak detection system with the help of ultraviolet light sensitive powder.

iv) Use of "Clean on demand system". This is latest concept of pulsing bags only when sufficient pressure drop is reached to save on installed air and enhance bag life. GNFC has gone a step further by installing a transmitter and controlling pulsing of bag through DDCS with dynamic indication of pressure drop.

v) Filter bag design changed from collar type to snap band type to eliminate leakages due to gasket failure/looseness.

vi) Replacing tube sheet with high precision holes with minimum tolerances in hole diameter to ensure proper bag fitness.

vii) Since the leak detection powder which was imported and hence costly at Rs. 15000 (circa USD 330) per can, import substitute was developed by synthesizing the U.V. sensitive powder at R&D centre of GNFC costing Rs. 2500 per can.

With all above measures implemented on 19.11.1998, following results achieved.

i) All the stack emission readings were below 100 mg/Nm^3 on consistent basis.
ii) Very high continuity and consistency operation of flash dryer system even at higher loads.
iii) Significant reduction in number of interruptions.
iv) Operation at low pressure drop 70-80 mmWC on consistent basis which ensures smooth operation of system.
v) No permanent blinding of bags experienced to-date. Inspite of sticky wet lime feed, it was possible to revive the bag filter performance completely with 1/2 an hour of idle pulsing.
vi) No maintenance requirement to-date.

ELIMINATING BLOWER VIBRATION PROBLEMS:

In the calcium ammonium nitrate plant, GNFC faced the problem of high vibrations in two blowers namely 50K003 fan for drying drum and 50K007 (CAN cyclone exhaust blower). The main reason for vibrations was found to be dust deposits inside impeller vanes causing imbalance and high vibrations. This necessitated plant stoppages and caused a down time of 154.98 hours in 1997-98 equivalent to 3228 MT CAN production.

As an innovative measure, it was decided to install acoustic horn first on 50K003 blower. Acoustics is a totally a new technological concept being employed for solving problems related to build up/deposits of solid particulate. An acoustic system consists of a pneumatically operated sound generator which produces controlled low frequency band with designated sound pressure level.

This energy is not destructive to solid structures and mechanical connections as the frequency is above the natural frequency of structures.

The sound variation is a fluctuation in local air pressure in the immediate vicinity of the horn. Due to this, solid particles resonate broke and fell down. This technique has been widely employed by USA companies and is also vastly improved in Finland by Nirafone Oy in association with the University of Helsinki.

Accordingly an acoustic system was procured from Harley Nirafone India Pvt. Ltd. and installed on 19.11.98. Within one month, it was made fully operational and as a result since then, there has been only one occasion of stopping plant due to high vibrations 3rd May 1999 (with total down time of 3 hrs.).

Thus acoustic horn has overcome problem of high vibration as well as having reduced effluent generated while cleaning the blower.

FUTURE ACTIONS:

In order to achieve consistent normal results with respect to emission of particulate matter, even during abnormalities like start-ups, shutdowns and disturbance in process, GNFC would install wet scrubbing system for both ANP and CAN plants and is likely to be commissioned by early 2001. This system for ANP will utilize the lean discontinuous effluent as scrubbing medium which is presently sent to effluent treatment plant. The scrubbed liquid will be concentrated in new evaporation system thereby producing suitable slurry for recycling to process. In short, discontinuous effluent stream will be fully recycled to process after ANP dust scrubbing and evaporation.

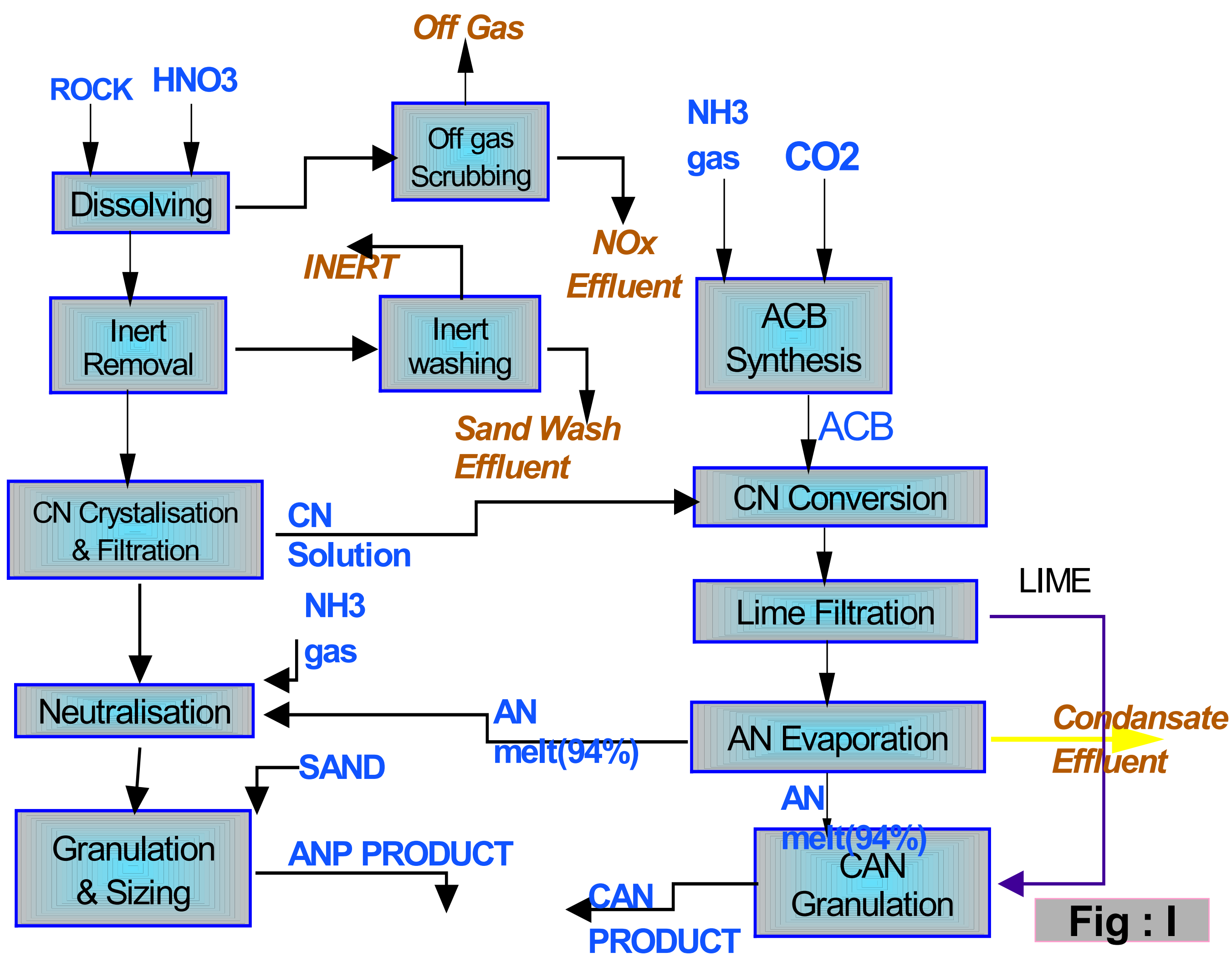
For CAN Plant, the AN condensate stream will be utilized as a scrubbing medium. The bleed from the wet scrubbing system being very small in quantity will be recycled to CN conversion section of ANP plant.

Hence after implementation of above mentioned wet scrubbing system for ANP and CAN plants, there will be drastic reduction in discontinuous and AN condensate effluent streams which will in turn reduce the cost of its treatment.

CONCLUSION:

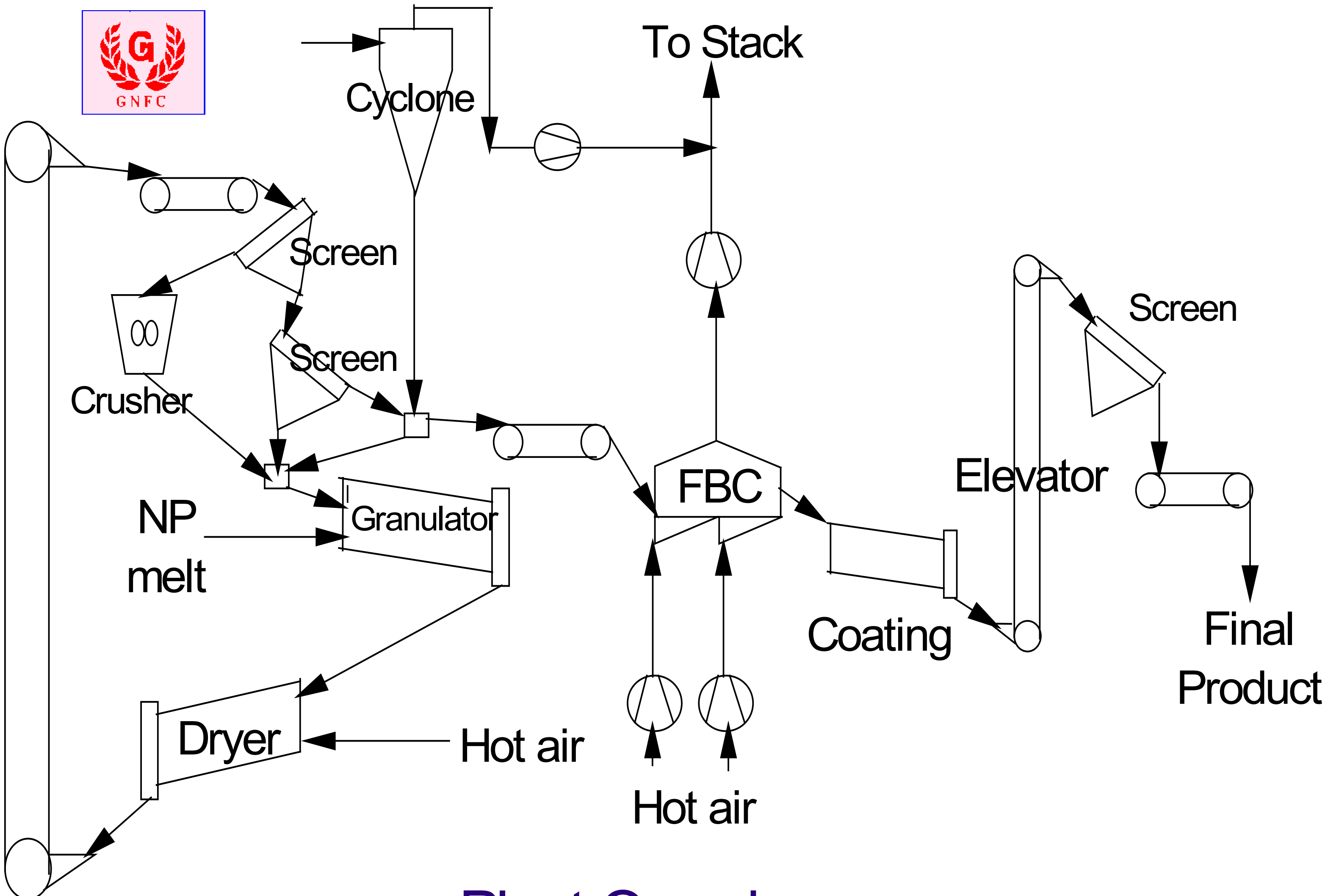
The nitrophosphate plant generates two types of effluents (a) liquid effluents from the ODDA Section (b) gaseous emissions from the dry sections. The thrust for controlling liquid effluents was two folds viz. reduction in quantity as well as reduction in nutrient loading. Beneficial results were achieved through in-house innovations mainly by modifying operating philosophy and by modifying the systems for collection and recycling of effluents.

For controlling gaseous emissions, the Company has adopted available technological advancements which have not only helped in controlling the emissions to the environment but also indirectly improved the production levels and continuity of the plants.



ROCK
HNO3
Dissolving
Off Gas
Off gas Scrubbing
NOx Effluent
INERT
Inert Removal
Inert washing
Sand Wash Effluent
NH3 gas
CO2
ACB Synthesis
ACB
CN Crystalisation & Filtration
CN Solution
CN Conversion
Lime Filtration
LIME
NH3 gas
Neutralisation
AN melt(94%)
AN Evaporation
Condansate Effluent
SAND
AN melt(94%)
Granulation & Sizing
ANP PRODUCT
CAN PRODUCT
CAN Granulation

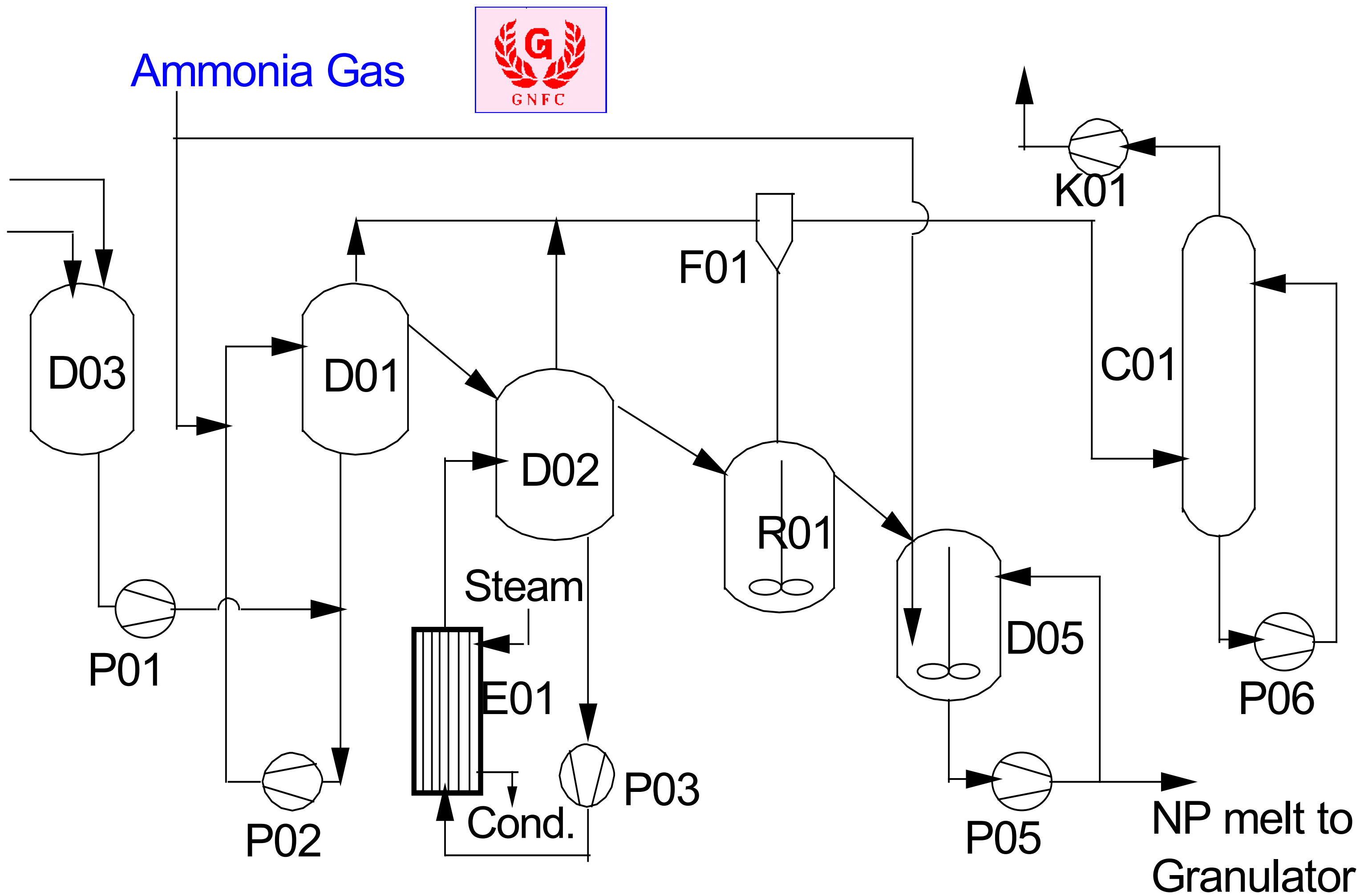
Fig : I



Plant Overview

Granulation / Drying / Cooling Unit

Fig : II



Plant Overview - Neutralisation Unit

Fig : IIa

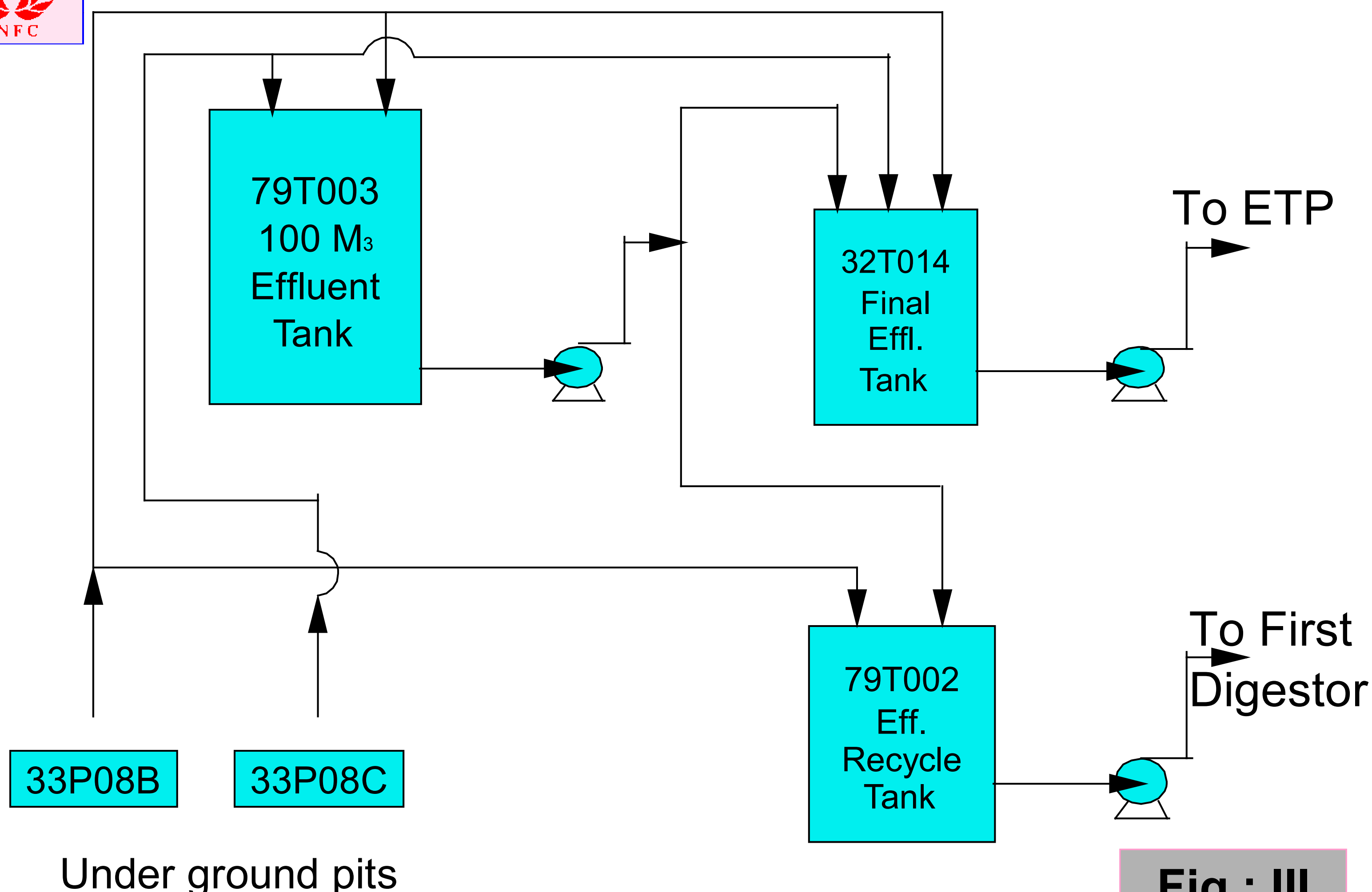
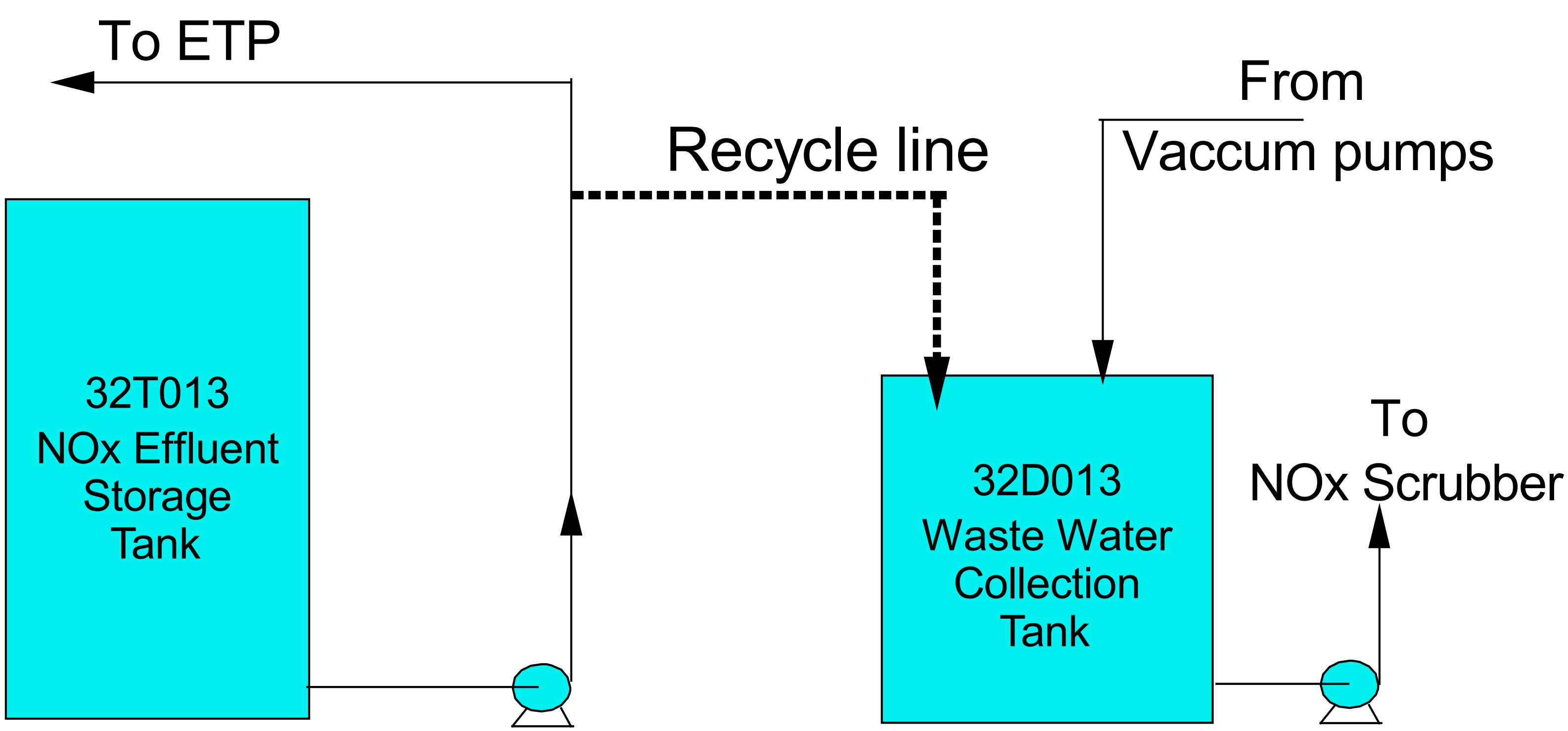


Fig : III

Reduction in Discontinuous Effluent



Reduction in NOx Water Effluent

Fig : IV

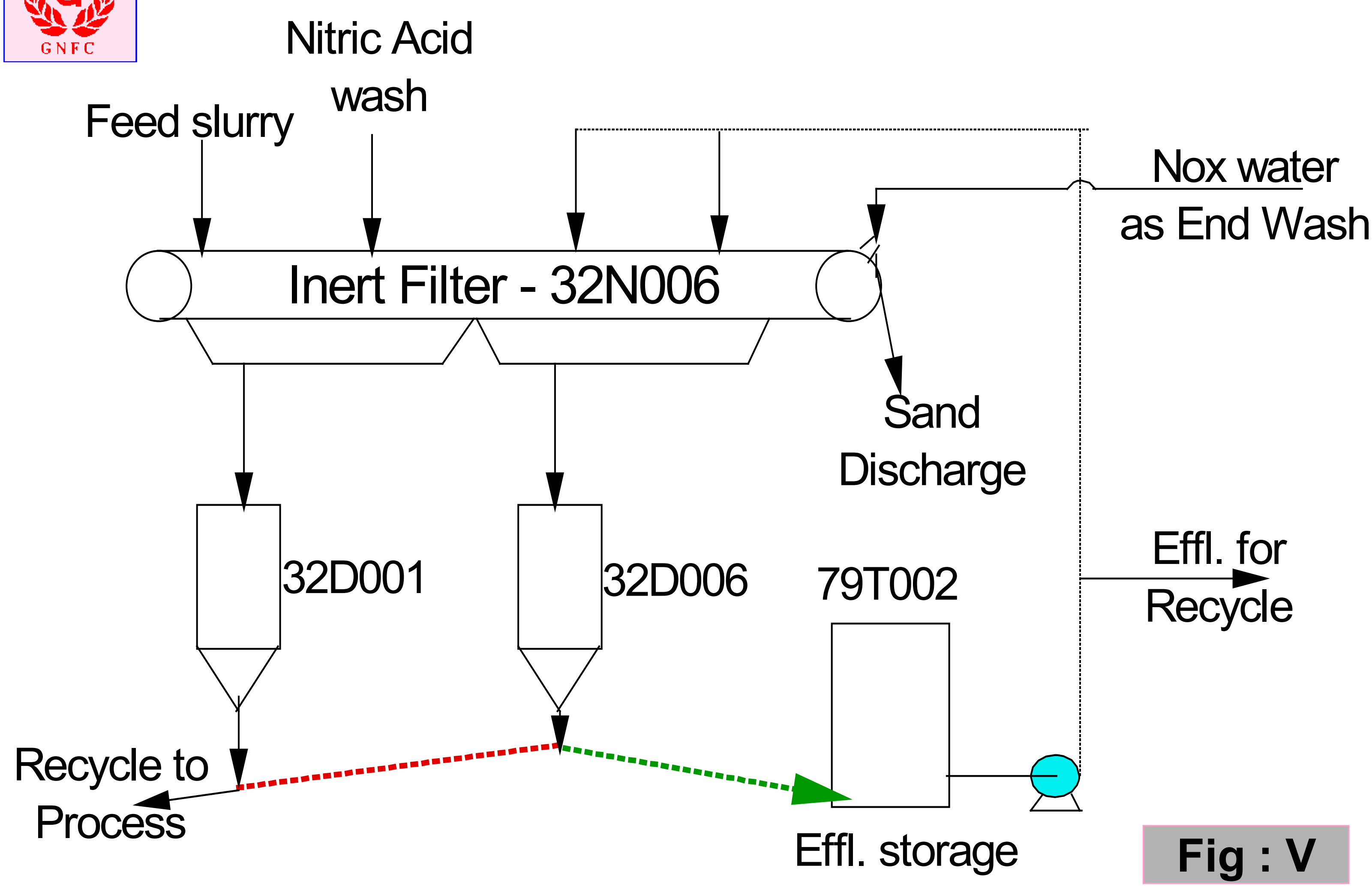
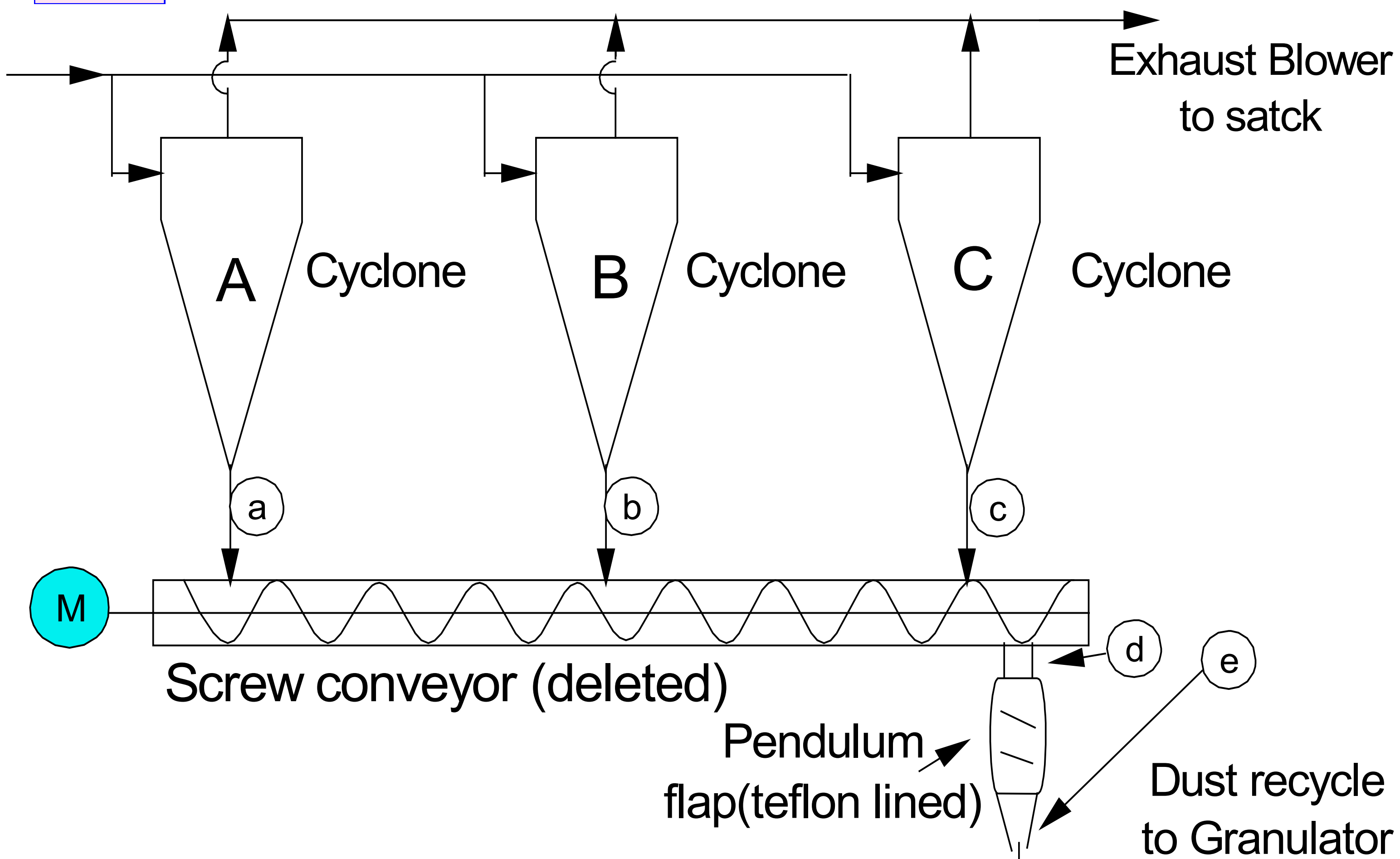


Fig : V

Recovery of Nutrient from Sand Wash Effluent



Cyclone System Modification

Fig : VI