International Fertilizer Industry Association

IFA Technical Conference

New Orleans, Louisiana, USA

1-4 October 2000

International Fertilizer Industry Association - Secretariat: 28 rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

OPERATING EXPERIENCE WITH DIFFERENT ROCK PHOSPHATES IN NITROPHOSPHATE COMPLEX

V.S. Joshi and P.A. Shah
G.N.F.C. Ltd, India

Gujarat Narmada Valley Fertilizers Co (GNFC) Ltd exploite l'atelier d'attaque nitrique avec le procédé ODDA depuis 1990. La technologie a été fournie par BASF Allemagne et l'engineering par UHDE (maintenant KRUPP-HUDE). La voie nitrophosphate fournit une intéressante avenue pour la production d'un engrais complexe agronomiquement équilibré.

Le phosphate brut étant la principale matière première, sa qualité a une importance primordiale pour une bonne marche du procédé et le maintien de la qualité des différentes étapes intermédiaires. Le phosphate étant un produit d'extraction minière entraîne avec lui un cortège d'impuretés. Tandis que la majorité des impuretés sont une gêne, certains ont un effet favorable sur le procédé d'attaque nitrique. La première partie de l'exposé traite des paramètres opérationnels à mettre en œuvre pour traiter le phosphate de différents origines et ceci est réalisé au mieux grâce à l'expérience de l'emploi systématique de différents phosphates.

Des phosphates de différentes origines montrent des comportements nettement différents bien que leurs constituants principaux puissent être semblables. Faire marcher la cristallisation – filtration de nitrate de calcium et l'ammoniation d'acide NP dans le procédé d'attaque nitrique sont très sensibles aux variations de phosphate brut. Différentes séries de paramètres opérationnels doivent être fixées pour traiter les phosphates d'origine diverses et ceci se fait le mieux grâce à l'expérience acquise par emploi systématique de différents phosphates.

Le point fort de cet exposé est de présenter l'expérience opérationnelle d'un atelier d'attaque nitrique avec différents types de phosphate. Des minerais de Jordanie, Israël, Afrique du Sud, Nauru, Floride, etc, ont été employés jusqu'ici. La deuxième partie de l'exposé souligne la méthodologie employée pour différents phosphates bruts et le comportement typique de chaque minerai vis à vis du procédé d'attaque nitrique et la conclusion tirée après chaque expérience.

ABSTRACT:

Gujarat Narmada Valley Fertilizers Co. (GNFC) Ltd. has been operating its nitrophosphate plant based on the ODDA process since 1990. The technology has been supplied by BASF Germany and engineering by Uhde (now Krupp-Uhde). The nitrophosphate route provides an interesting avenue for producing an agronomically balanced complex fertilizer.

Rock phosphate being the main raw material, its quality is of paramount importance for smooth functioning of the process and maintaining quality of various intermediate streams. Rock phosphate being a mined product brings along with it a host of impurities. While most impurities are a hindrance, some impurities give a positive effect on the nitrophosphate process. The first

E-mail : admodashia@gnvfc.guj.nic.in

part of this paper deals with our operational experience with effect of various impurities of rock for the nitrophosphate route.

Rocks from various origins show distinctively different behaviour even though their major constituents may be similar. The operation of calcium nitrate crystallization and filtration and the ammoniation of NP acid in the nitrophosphate process are very sensitive to changes in rock phosphate. Sets of operating parameters need to be established for processing rocks from diverse origins and this is best achieved from experience by systematic use of different rock phosphate.

The main thrust of this paper is to present the operating experience of nitrophosphate plant with different types of rock phosphate. Rocks from Jordan, Israel, South Africa, Nauru, Florida, etc. have been used so far. The second part of the paper highlights the methodology employed for using these rocks, typical behaviour of each rock vis-a-vis the nitrophosphate process and the conclusion derived after each experiment.

1.0 INTRODUCTION :

Gujarat Narmada Valley Fertilizers Company is one of the world's largest single stream fuel oil based ammonia and Urea Complex located in India's one of the fast growing industrial zone at Bharuch - Gujarat. GNFC started it's operations with 1350 MTPD ammonia and 1800 MTPD urea plants in January 1982. After stabilizing the operations of both the plants at more than their nameplate capacity, the Company has expanded its operation for phosphatic fertilizers (ANP-CAN) and industrial chemicals like weak nitric acid, concentrated nitric acid, methyl formate, formic acid, acetic acid, methanol, aniline and TDI. Along with above chemical plants, the company has also diversified in the electronic field for production of PCB, RAX and PAX.

2.0 NITROPHOSPHATE COMPLEX :

The Nitrophosphate Complex of GNFC comprises of an integrated ammonium nitrophosphate (ANP) and calcium ammonium nitrate (CAN) fertilizer plants each having a capacity of 475 MTPD. A 630 MTPD weak nitric acid plant supplies nitric acid for captive consumption and is also used to operate a 100 x 2 MTPD conc. nitric acid plant.

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

The main steps of the 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.(NP acid).
d) Ammoniation i.e. neutralization of NP acid.
e) Granulation of the slurry and conditioning of the product.
f) Conversion of CN crystals to lime and ammonium nitrate.
g) Concentration of ammonium nitrate.

Calcium carbonate and ammonium nitrate are produced as by-products in 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 itself for N2:P2O5 ratio correction. A small quantity of sand separated from rock phosphate is recycled back as a part of the filler with main stream of the sand added in granulation section.

The schematic block diagram of ANP process highlighting all the sections for ODDA process is shown in Figure-1. The Table 'A' below indicates the rise in production level since commissioning i.e. year 1991-92.

TABLE-A

Year	ANP		CAN	
	Production	**Cap.Uti. %**	**Production**	**Cap.Uti. %**
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
1997-98	155,704	109	170,738	120
1998-99	150,812	106	152,689	107
1999-2000	155,889	109	129,143	90

A) **Effect of rock phosphate impurities on Nitrophosphate Process:**

During the operation of the nitrophosphate plant for the last 9 years, the effects of various rock impurities on the process have been studied in detail. The role of main constituents of rock is summarized below:

1) **P_2O_5 - Phosphorous pentoxide:**
The most important constituent of rock phosphate is P2O5 as this is the element required for fertilizer production. The ODDA section of our nitrophosphate plant is designed for a minimum P2O5 content of 33.4%. Hence any rock having P2O5 content lower than 33.4% is not suitable as it will increase the hydraulic load of the plant which has to be removed before granulation. Higher P2O5 rocks are beneficial as the impurities level in these rocks will be lower.

2) **Chloride**s**:**
High amount of soluble chlorides severely increases the rate of corrosion. Hence it is preferable to have a rock with as low chloride content as possible. The chloride content in no case should exceed 300 ppm. At this level of chloride, plant equipments are designed for 20 years of life.

3) **Silica:**
The silica content of the rock is in two forms. The active silica (clay) is beneficial as it reacts with fluorides in the rock and produces flousilicates which due to the low solubility, readily precipitates and finally reduces corrosion.

The other silica (quartz) is inert which will not affect the process chemistry, but causes erosion in the various digestor section equipments. Hence the rock should have sufficient quantity of active silica to fix fluorides while the inert silica should be minimum. For this, it is recommended to have active silica/fluoride ratio of 0.5 and the total silica should not exceed 3%.

$6HF + SiO_2 \text{ ----> } H_2SiF_6 + 2H_2O$

4) **Fluoride:**
Only marginal quantity of fluorine vents to vapour stream and major fraction of fluoride travels along with NP slurry, so to fix the fluoride, minimum quantity of active silica should be available.

5) **Al_2O_3/Fe_2O_3 (aluminium/iron oxide):**
A certain amount of these oxides are required for achieving good calcium nitrate crystal growth and favourable lime size for filtration. However, higher amount of R_2O_3 causes very coarse lime which is not suitable for CAN plant and it also increases viscosity of the nitrophosphate melt in ANP plant causing load reduction and small reduction of water solubility of P_2O_5.

R_2O_3 content of 0.4% ~ 0.8% is most favourable for ideal crystal growth of calcium nitrate as well as favourable lime size distribution.

6) **MgO (magnesium oxide):**
Acid soluble magnesium seems to be the main rock impurity that causes an increase in viscosity during ammoniation of NP melt. It should be as minimal as possible. MgO content above 0.3% in rock is detrimental for the process.

7) **Organic matter**:
Higher organic matter in the rock causes excessive foaming and NOx emission during digestion. This makes the rock difficult to handle and restricts the load of the digestors. Antifoam which uses to suppress the foams, will hinder the growth of CN crystals.
Organic matter should not exceed 0.3%.

8) **Moisture**:
Higher moisture content will increase water in NP acid and reduces the effluent recycle into system.

9) **Size:**
The size of the rock phosphate should be such that it does not create dust pollution and unnecessary crushing it. The ideal size is 1 to 4mm 85%. Size has impact on reactivity of rock phosphate.

10) **Carbon:**
External contamination of the rock with carbon (coal) causes hazardous situation. Carbon particles carry up to KAN solution and decomposition of ammonium nitrate. It should be nil.

METHODOLOGY FOR ROCK PHOSPHATE PROCESSING AND EVALUATION:

For any rock phosphate, about 10 - 12 standard parameters are analyzed and based on the level of different impurities, a broad prediction of its behaviour is made. The analysis is compared with standard specification sheet (Annexure-I) and only those rocks whose analysis is conforming to exactly as per our requirement are cleared for further trial. The rock sample of Syrian, Algerian, Chinese, etc. have been rejected due to above criterion.

The behaviour of the rock is also dependent on the geographical location of the mines. Hence it may happen that two rocks which are more or less similar in specification but mined from geographically different locations may exhibit typically different behaviour. Silica hardness, and other impurities are the few factors.

From R&D trials of rock whose specifications are matching with our requirement general ideas about behaviour of rock during actual operation is obtained.

The actual trials in the plant is carried out in a phase-wise manner by blending of 10% of trial rock with the main rock. The plant parameters are monitored and adjusted and the blend ratio is increased in steps of 10% after minimum observation at least for one month. The changed parameters are recorded for future use. This practice is also followed internationally by phosphatic fertilizer producers, while changing over the source of rock.

Many a times blending of rocks helps in maintaining other parameters and the blended rock is more suitable than the two original rocks, if used independently.

HISTORY/EXPERIENCE OF DIFFERENT ROCKS USED IN GNFC NITROPHOSPHATE PLANT:

- The nitrophosphate plant was commissioned in 1990 using Jordan rock.
- The following rocks used in plant to-date (Annexure-II).
- The total annual consumption of rock is @ 100, 000 MT

1) **Jordan** : Period of use - 1990 - 2000 (use continued).
Quantity used : @ 800, 000 MT

- ❖ Jordan rock has been used in the plant since commissioning.

- ❖ After adjusting the operating parameters during the initial 2~3 years of operation, the plant operation with 100% Jordan rock is well established and due to this it is possible to run the plant on high loads on a sustained basis.

- ❖ Presently with 100% Jordan rock, we are achieving an average production level of above 550 MTs on a continuous basis.

- ❖ The record of operation for 47 days continuous run without cleaning was also established in November - December 99. Earlier plant cleaning was required every 15~20 days.

- ❖ Parameters for smooth operation of both ANP and CAN plants have been well established with Jordan rock.

- ❖ Jordan rock with low R_2O_3 (0.30%) was used by allowing the crystallizers to cool with slow rate to increase the size of CN crystals. Earlier we were facing problem of finer CN crystals with low R_2O_3. By successful implementation of this innovative idea, the limitation could be overcome.

2) **Florida** - Period of use : 1991-1994
Quantity - 50,000 MT

- ❖ The very first consignment of Jordan rock contained very high chlorides. Hence Florida rock was procured immediately after commissioning for blending with Jordan to bring down level of chlorides.

- ❖ Subsequently chloride problem was solved in Jordan rock but when Florida blending was stopped, plant could not be run on 100% Jordan rock due to problems and load limitation in CN filtration/lime filtration.

- ❖ Jordan/Florida blend was used upto 1993 and plant was operation was stabilized with a blend of 80/20 Jordan/Florida giving best results.

- ❖ By changing cooling pattern in crystallizer as highlighted earlier, the blending of Florida was stopped as cost was high and plant operation was again established with 100% Jordan rock. Saving of @ $ 222,000 per annum was achieved by stopping Florida rock blending.

3) **Morocco:** Period : March - April 92
Quantity : 1000 MTs

- ❖ The rock was used in 1992 as a stop-gap arrangement during non-availability of Jordanian rock.

- ❖ As the plant was under stabilization in this period and it was used 10% with Jordan and Jordan/Florida mixture, concrete conclusion for the rock could not be established.

- ❖ However, there was no adverse effect noticed with 10% ratio.

- ❖ From the specification of Morocco rock available with us, the rock appears suitable for trial in the plant. No adverse effects have been observed while testing this rock in R&D trials.

4) **Israel :** Period : July 93
Quantity used : @ 2500 MT

- ❖ Total 5000 MT was procured and trial taken in July 93. Due to non-availability of Jordan and other rock, trial was started with directly 100% Israel rock. However, due to severe granulation problem in CAN Plant, trial was discontinued after 15 days consuming 2500 MT of rock.

i. In digestion section, initially temp. went up as high as 76^{o}C which was controlled by further cooling of nitric acid.
ii. Digestor agitator current was found increased from 20 ---> 25 A.
iii. CN crystals size was big, similar to Florida.
iv. P2O5 in KAN was 0.15 ~ 0.10%.
v. Though CML remains viscous filtration was very good which was not the case with the Jordan rock.
vi. Lime size is very coarse.
vii. CAN plant granulation was not picking up with by product lime.

- ❖ Rock was very fine causing higher dusting and caused irritation in the eyes during reclaiming.

- ❖ The behaviour of the rock in the ODDA was found satisfactory except high temperature in digestor.

5) **Senegal:** Period : October - November 92
Quantity - 5000 MT.

- ❖ Senegal rock was used intermittently in 1992-93.

- ❖ Severe increase in corrosion and difficulties in sand separation were experienced with this rock.

- ❖ Choking tendency of ANP granulator had also increased whenever Senegal rock was processed

6) **Foskor :** Period : July - September 94
Quantity - 5000 MT

- ❖ About 5000 MT of Foskoor (South African) rock was processed between July-September 1994.
- ❖ Trial was started with 10% blending with Jordan rock phosphate for one month and then increased to 20%.
- ❖ Plant performance was good and no remarkable adverse effects were observed.
- ❖ Active silica level was found low.
- ❖ During further trial, we may increase the blend ratio further in a gradual manner, if our requirement of active silica is satisfied.

7) **Nauru:** Period : 1998-99.
Quantity - 16,000 MT

- ❖ A total of 16,000 MT Nauru rock was processed in various spells in 1998-99.
- ❖ Blending was started in 20% ratio with Jordan rock phosphate and then increased to 30%.
- ❖ Blending ratio could not be increased further due to limitation of active silica and coarse size of the rock. (Limited capacity of the rock gridning unit).
- ❖ Initially problems were faced in neutralization unit of ANP plant but after the operating parameters were gradually modified, smooth operation upto 30% blend ratio could be achieved.
- ❖ Digestor agitated blades erosion noticed.
- ❖ More effluent recycle was possible due ot higher P2O5 in the rock phosphate.
- ❖ Higher foaming observed in the digestor.
- ❖ No problem of viscous CML was encountered even when crystallizer agitator current was >65A. Filtration gets disturbed under similar condition with Jordan rock phosphate.

- It is possible to increase the blend ratio higher than 50%, if requirement of active silica and size are satisfied.

CONCLUSION:

The Nitrophosphate Complex at GNFC is unique in the sense that ammonium nitrophosphate and calcium ammonium nitrate plants are integrated with each other. The quality of rock processed affects directly the slurry behaviour in the ANP plant as well as the quality of byproduct lime from the ANP plant which is used as raw material for the CAN plant. The choice of rock phosphate and adjustment of parameters while processing it have to therefore delicately balance the requirements of both.

While the operation of the Nitrophosphate Complex is well established with Jordan rocks over the years, we have been also successful in blending other rocks in various proportions in a controlled and scientific manner. Efforts to establish plant operation with different rocks will continue in the future to achieve the best techno-economic benefits.

ANNEXURE-II
DETAILS OF VARIOUS ROCKS PROCESSED

Sr. No.	Rock type	Quantity used (in MT)	Ratio with Jordan	Period of use
1	Florida	50,000	50%	1991
			20%	1992/1993
2	Senegal	5,000	30%	Oct/Nov. 92
			100%	Nov./Dec. 92
			100%	July 93
3	Morocco	1,000	20%	May/June 92
4	Israel	2,500	100%	July 93
5	Foskor	5,000	10%	Aug. 94
			20%	Sept. 94
6	Nauru	16,000	20%	Feb/March 98
			30%	Mar-June 98
			30%	Sept.-Nov. 98
			20%	June Aug. 99

ANNEXURE-I

COMPARATIVE STATEMENT OF ANALYSIS OF DIFFERENT ROCKS USED BY GNFC

Sr. No.	Constituent	GNFC Spec.	Jordan %	Florida %	Morocco %	Senegal %	Israel %	Foskor %	Nauru %
1	P2O5	33.4% max.	33.6	33.0	33.1	36.40	33.30	39.80	38.00
`2	Chlorides	300ppm max.	250 ppm	100 ppm	435 ppm	85 ppm	264 ppm	213 ppm	60 ppm
3	Total Silica	3.5% max.	3.3	3.2	1.8	3.00	2.80	0.47	0.10
4	Active Silica	2.0% min.	2.1	1.4	===	===	1.50	0.44	0.10
5	Fluorides	3.9% max.	3.6	3.0	3.3	3.50	3.40	1.70	2.60
6	AL_2O_3	0.4% min.	0.3	1.4	0.9	0.85	0.55	0.17	0.19
7	Fe_2O_3	0.8% max.	0.2	1.1	0.2	0.75	0.40	0.18	0.17
8	MgO	0.3% max.	0.2	0.3	===	===	0.22	0.26	0.17
9	Org. C	0.3 max.	0.2	0.1	0.0	0.13	0.13	0.06	0.10
10	Ratio Active Silica to Fluoride	0.5 min.	0.6	0.5	===	===	0.44	0.26	0.05

BLOCK DIAGRAM OF ANP / CAN PROCESS

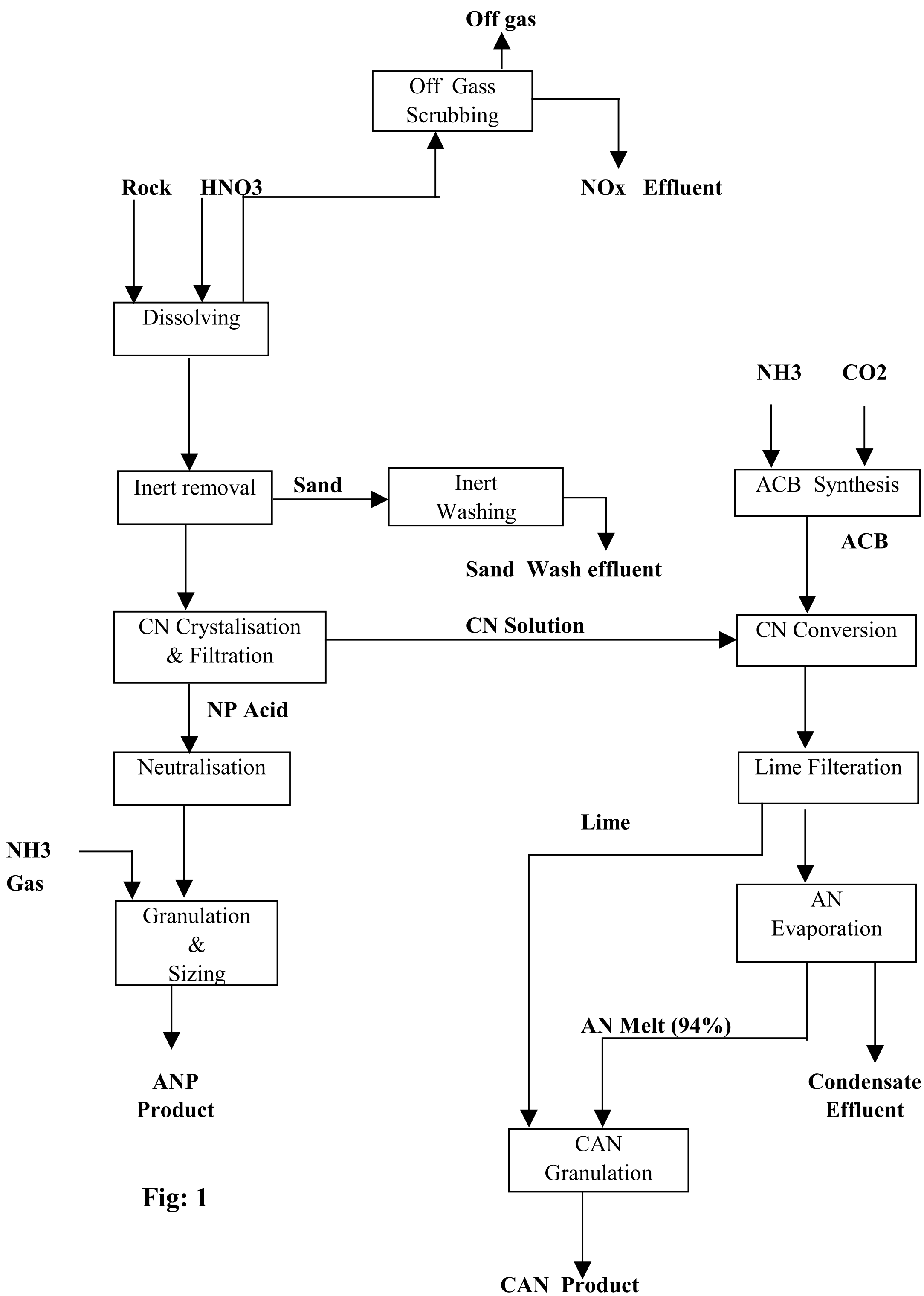
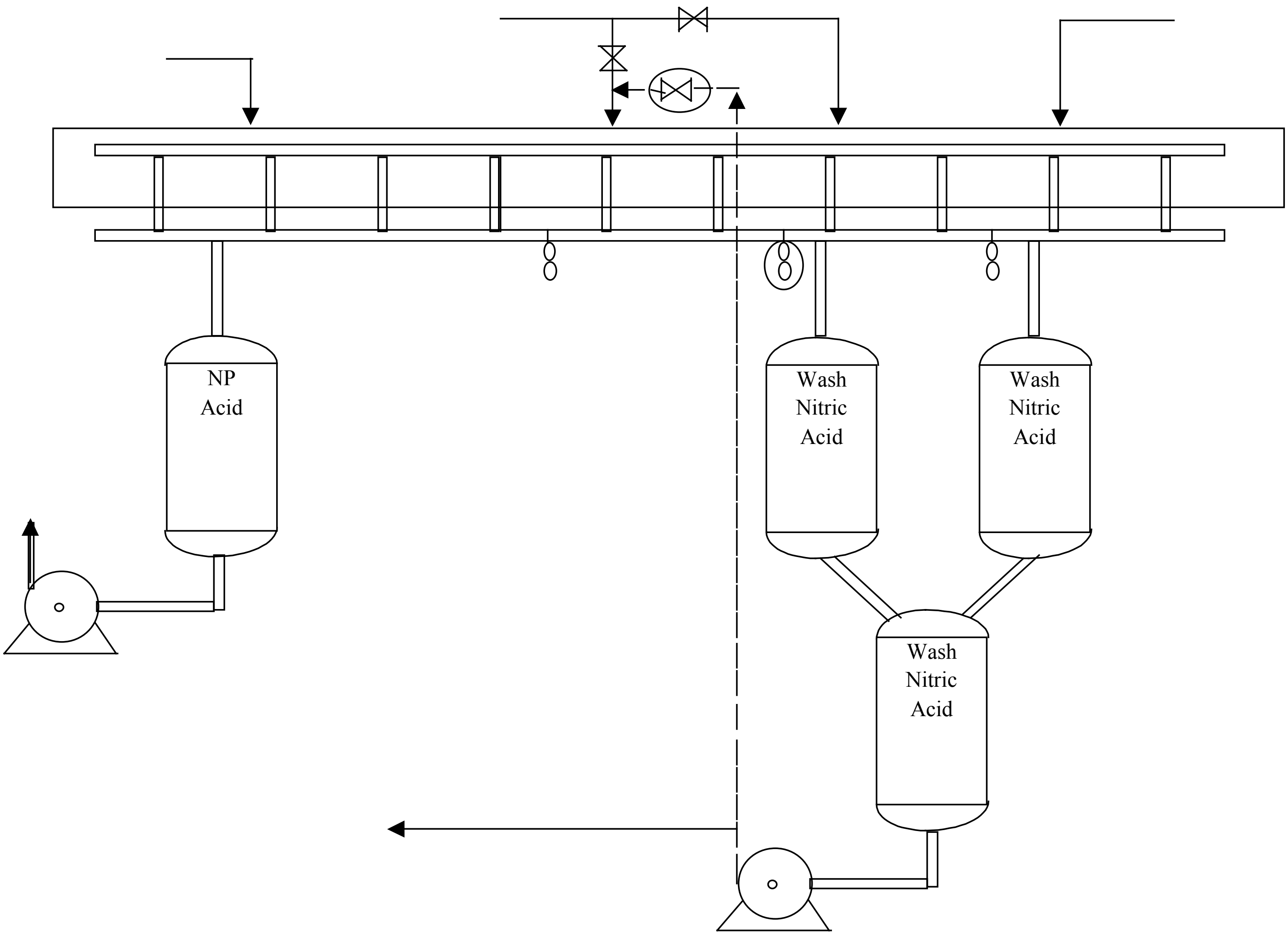


Fig: 1


NP
Acid
Wash
Nitric
Acid
Wash
Nitric
Acid
Wash
Nitric
Acid