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TECHNOLOGY UPGRADATION BY BREAKTHROUGH INNOVATIONS GNFC EXPERIENCE WITH NITROPHOSPHATE ODDA PROCESS[1]

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SUMMARY

The nitrophosphate complex of GNFC Ltd., Bharuch, Gujarat (India) was commissioned in 1990. The technology is based on the Odda process supplied by BASF, Germany.

The nitrophosphate route for the manufacture of complex fertilizers is a concept which is relatively new to India and therefore has a vast potential during the phase of commissioning and technology absorption. A deep insight has been gained in the technology of Odda process leading to major innovations in the basic technology itself.

This article highlights our experience with the Odda process and the major innovations implemented which have resulted in upgradation of the Odda technology. The insight gained in the process is also discussed which has helped to create adaptability of the process to different grades of rock phosphate, our main raw material.

RESUME

Le complexe de production de nitrophosphate de GNFC Ltd à Bharuch, Gujarat, (Inde), a été réceptionné en 1990. La technologie repose sur le procédé Odda et a été fournie par BASF, Allemagne.

La voie nitrophosphate pour la fabrication d'engrais complexes est un concept relativement nouveau en Inde et a, par conséquent, un vaste potentiel. Durant la phase de réception et d'absorption de technologie, une connaissance approfondie a été acquise dans la technologie du procédé Odda aboutissant à des innovations majeures dans la technologie de base elle-même.

L'exposé met l'accent sur notre expérience du procédé Odda et les innovations majeures, mises en oeuvre qui ont entraîné une amélioration de la technologie Odda. La connaissance du procédé est également discutée ; elle a permis de créer l'adaptabilité du procédé pour les différentes qualités de phosphate, notre principale matière première.

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1. INTRODUCTION

Gujarat Narmada Valley Fertilizers Company (GNFC) is one of the world's largest single stream fuel oil based ammonia and urea complex located in India's fast growing industrial zone at Bharuch - Gujarat. GNFC started its operations with 1350 MTPD ammonia and 1800 MTPD urea plants in January 1982. After stabilising 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 WNA, CNA, methyl formate, formic acid, acetic acid, methanol, aniline and TDI. Along with above chemical plants, the company has also diversified into the electronic field for production of PCB, RAX and PAX.

2. NITROPHOSPHATE COMPLEX

The Nitrophosphate technology was developed in the 1930's on the Odda patents by Erling Johnson. This technology does not require sulfur or sulfuric acid. Instead, nitric acid is used for the digestion of rock phosphate. The process requires CO_2 and therefore it is beneficial to have integration with an ammonia plant for a steady supply of CO_2. The only so called waste or by product of this process is calcium carbonate which has a variety of applications in agriculture and chemical industry.

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[1] *Amélioration de la technologie par des percées innovatives - Expérience de GNFC avec le procédé d'attaque nitrique Odda*

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 MTPD conc. nitric acid (CNA) 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 schematic block diagram of the nitrophosphate complex and Odda process is shown in Figure 1.

Rock phosphate is dissolved with dilute nitric acid (60~62%) in a series of digestors. The dissolving solution which mainly consists of phosphoric acid, calcium nitrate and excess nitric acid is treated for sand removal. It is then crystallized in batch crystallizers to separate calcium nitrate as tetrahydrate crystals. The crystals are filtered off and washed to remove the adherent phosphoric acid/nitric acid. The mother liquor is called NP acid and is neutralized with ammonia in 2 stages and granulated to get ANP granules.

The filtered calcium nitrate crystals are dissolved in a dilute ammonium nitrate solution (60%) to form a calcium nitrate (CN) melt. The CN melt is reacted with synthetic ammonium carbonate (ACB) in the CN conversion reactors to form ammonium nitrate (60%) and calcium carbonate. The calcium carbonate is filtered from the slurry, washed and disposed off as a byproduct. The ammonium nitrate solution is concentrated in an evaporation unit to a melt having a concentration of 94%.

Synthetic ammonium carbonate is produced by reacting ammonia gas and carbon dioxide (CO_2) in a circulating liquid phase (Messerberg reaction).

The 94% AN melt and calcium carbonate which are both byproducts of the ANP plant are used as raw material for the production of CAN fertilizer. The excess calcium carbonate not utilized by CAN is sold as a by-product.

3. THE NEED FOR INNOVATIONS

The Odda Plant was commissioned in August 1990. After the initial phase of stabilisation which continued for about 2 years, the thrust was put on debottlenecking and improving capacity utilisation. Based on the operating experience and the insight gained in the process by in depth study of various parameters, major technological innovations were carried out which have led to increased productivity and capacity utilisation. The innovations covered the following major areas.

3.1 Increasing throughput of the plant without any major capital expenditure.

3.2 Overcoming the problems of filtration and capacity utilisation with low R_2O_3 (Al_2O_3 + Fe_2O_3) rocks.

3.3 Reducing the interdependency of the ANP plant with the CAN plant which operated on the byproducts of the ANP plant.

3.4 Maximum recovery of nutrients by recycling max. effluents back to the process without affecting quality.

The breakthrough innovations which have led to the upgradation of the technology are described below.

4. RADICAL CHANGE IN CONCEPT OF WASH ACID RECYCLING

The calcium nitrate crystals produced by cooling in crystallizers are separated on a horizontal vacuum belt filter. For recovering the adherent dissolving solution on the crystals, a wash of cold nitric acid is given to the cake. This nitric acid after washing the cake generates a wash acid stream which as per the Odda process was totally recycled back to the digestors.

For running the plant at higher loads, sufficient NP acid from the CN filter was not available due to limitations in the capacity of CN filter.

An analysis of the quality of wash acid revealed that it had essentially the same CaO/P_2O_5 ratio in NP acid as it contained a mixture of nitric acid and the NP acid washed from the filter cake. The total recycle of this wash acid was restricting the throughput of the digestors and the CN filtration units.

As a radical step it was decided to mix. a part of this wash acid stream (~50%) directly to the NP acid. This would serve two purposes:

1. Increase the generation of NP acid without affecting its overall quality.

2. Increase the throughput of digestors and CN filtration units without any capital investment.

The modification was implemented by making minor changes in the configuration of the CN filter (see Figure 2).

The above modification resulted into the following major gains:

1. Increase in production capacity of ANP by about 50-75 MT/day with the same loading on the CN filter.

2. Increase in throughput of digestor as the unnecessary recycle of P_2O_5 by means of wash acid was avoided.

3. Energy conservation in refrigeration of brine solution and heating of nitric acid.

4. Reduction in effluent quantity by creating more avenues for effluent recycling.

Thus by incorporating a radical change in the concept of wash acid recycling, we have been able to achieve an increase of 10-15% P_2O_5 throughput in the process.

5. OVERCOMING THE PROBLEM OF FILTRATION BY TECHNOLOGICAL INNOVATION

The ANP Plant of GNFC was commissioned using Jordan Rock. Typical Jordan Rock contains very low R_2O_3 content (0.25-0.30%). Initial plant operation was at low loads (70-80%) due to teething commissioning problems normally associated with such slurry into the operation of CN filtration and Lime filtration.

However, as plant load started picking up, problems started surfacing, very fine CN crystals were causing disturbances in CN filtration and P_2O_5 losses remained high. Lime produced was also very fine causing choking in the lime filters and restricting plant load.

Blending with high R_2O_3 rock was started to combat the problem of filtration. Perceptible improvement was seen in CN crystals growth & the limitation of filtration of CN crystals was removed P_2O_5 losses also reduced due to improved washing efficiency. Lime size also became coarser removing the bottlenecks of lime filtration.

From the above following can be concluded.

1) Size of the CN crystals produced in the Odda section is a direct function of the R_2O_3 content of the rock used.

2) Size of lime particles produced during CN conversion is directly related to the size of the CN crystals.

3) The size fraction of lime below 45 microns caused problems of choking during lime filtration.

5.1 ROLE OF R_2O_3 IN CN FILTRATION

Calcium nitrate filtration and lime filtration operations form the heart of the Odda process. Good growth of CN crystals allows proper filtration and washing on the CN filter and proper removal of the phosphoric acid/nitric acid adhering to the CN crystals. The efficiency of P_2O_5 nutrient also depends upon maximum removal of P_2O_5 from calcium nitrate crystals slurry.

Improper washing of the cake, apart from increasing P_2O_5 losses also adversely interferes with the CN conversion reaction by forming very fine lime which is difficult to filter and wash. Both these operations therefore are very sensitive and control the load and nutrient efficiency of the entire plant.

It was found from our operating experience that both CN filtration and lime filtration are function of the R_2O_3 content (Al_2O_3 + Fe_2O_3) of the rock used.

Low R_2O_3 rocks (0.25%-0.30%) produced very fine CN crystals which were difficult to filter. Washing efficiency was also reduced leading to higher P_2O_5 losses. The lime produced from such crystals was very fine. Filtration of fine lime was difficult and plant load was restricted. High R_2O_3 (2-2.5%) produce very coarse CN crystals which can be very easily filtered. Washing efficiency is very high and P_2O_5 losses very low. The lime produced from such crystals is also very coarse. Lime filtration is very smooth and no load restriction is faced.

5.2 TECHNOLOGICAL INNOVATION - IDENTIFICATION OF NEW PARAMETERS

Though blending to achieve the desired R_2O_3 content solved the problem of plant operation, it created certain additional problems as listed below:

1. Higher operating cost due to the high R_2O_3 rock used for blending.

2. Inconsistent operation such as blending was manually controlled.

3. Higher inventory cost since two different rocks had to be maintained.

To eliminate the blending with high R_2O_3 rocks and to achieve the same favourable lime size distribution with low R_2O_3 rocks only, a novel idea was put into operation on an experimental basis.

The idea was "To increase the cooling time in crystallizers between super saturation and bulk crystallization". The aim was to initiate gentler seeding. The expected result was to generate coarser CN crystals without affecting the overall throughput of the plant.

The above idea was based on two observations:

1. Formation of coarser lime was found related to formation of coarser CN crystals during past experience with different rocks.

2. The lime size range with different rocks was found as below:

   a) Low R_2O_3 rocks (e.g. Jordan): 90% below 63 of which 40%-60% was below 45.

   b) Blend having avg. 0.7% R_2O_3 (e.g. Jordan/Florida 80/20 blend): 80-85% below 63 of which only 20-25% was below 63.

As the filtration problems were encountered only with the fraction below 45, the above idea was aimed at reducing the 45 fraction of lime with low R_2O_3 rocks only to a level similar to the 80/20 blend.

The implementation of the above idea was started on a trial basis in Sept'93 using 100% Jordan rock. The cooling time in the crystallizers between supersatuation and bulk crystallization was increased by adjusting the cooling brine flows to the crystallizers trains (Figure 3). No hardware modification was involved. The change in crystallization curve is shown in Figure 4.

The results of the trial run were exactly as anticipated. Extended cooling in crystallizers while using low R_2O_3 rocks resulted into formation of coarser crystals than with fast cooling using the same rock (Ref. table B1 for lime size data).

The behaviour of both CN filtration and lime filtration was found similar to that during the 80/20 blend.

Thus after our experience with various rocks and the above experiment, it has been conclusively established that though R_2O_3 content of the rock phosphate is basic parameter controlling the size of CN crystals and lime produced from the Odda process, the size can be manipulated within a certain range by modifying the cooling conditions in the crystallizers. Cooling rate in the crystallizers between supersaturation and bulk crystallization was thus identified as a new additional parameter for controlling the size of CN crystals and lime produced in the Odda process.

6. REDUCING INTERDEPENDANCY OF ANP AND CAN PLANTS

The CAN plant utilizes the byproducts of ANP plant viz. calcium carbonate (lime) and ammonium nitrate as the raw materials. Hence it is totally dependent on the ANP plant for maintaining continuity of operation.

The continuity of CAN plant was suffering and heavy production loss was being faced due to non availability of AN melt if there was any interruption in the ANP plant on following accounts.

1. Interruption in the Odda process due to its own internal problems or planned shutdown.
2. Non-availability of CO_2 from the ammonia plant.

6.1 NOVEL IDEA - UTILIZING ACB SYNTHESIS COLUMN FOR AN SYNTHESIS

In order to maintain continuity of AN availability during Odda section shutdown a novel idea of utilizing the ACB synthesis column for ammonium nitrate synthesis was put into operation.

The ACB synthesis column is designed to produce ACB solution by synthesis of ammonia and carbon dioxide (CO_2). The liquid phase is provided by circulation rate of 400 M^3/H of ACB solution and the heat of reaction is removed by cooling water in a plate type heat exchanger. During shutdown this system is cleaned by nitric acid circulation and then remains idle.

The same column was utilised for ammonium nitrate synthesis with the same hardware set up. The 1st nitric acid line which was meant for cleaning purpose was utilised as the source of nitric acid and the heat of reaction was removed by the same plate type heat exchangers (Figure 5). After successful synthesis of ammonium nitrate in the column the line size of nitric acid was modified to produce sufficient ammonium nitrate to operate the CAN plant at full capacity. The instrumentation logic was also made foolproof for continuous operation of the system either for ACB synthesis or AN synthesis.

The above innovation has made operation of the CAN plant totally independent of the operation of the ANP plant as well as non-availability of CO_2.

7. MAXIMUM RECOVERY OF NUTRIENTS

The main problem encountered was in recycling acid bearing effluents generated from the dissolving and CN filtration area. This was due to stringent water balance requirement of the digestors. Frequent attempts were made to recycle this nutrient bearing streams at various points in the process but were not successful even after reduction in quantity of the streams as the quality of the intermediate NP acid produced was getting disturbed sometimes even resulting into production loss.

By implementing following two changes, favourable conditions were created in the digestor for facilitating recycle of effluent streams rich in nutrients.

7.1 WASH ACID MIXING WITH NP ACID

This innovation has been described earlier. By mixing part of wash acid directly with NP acid, the water which was being recycled with wash acid back to digestors was reduced. This created an opportunity to put additional water in the digestors to maintain the same water balance.

7.2 INCREASE IN NITRIC ACID CONCENTRATION

The concentration of nitric acid produced in our WNA Plant was increased from 60% to 62%. The increase of concentration by 2% of acid fed to digestors created the scope of putting extra water in the digestors without affecting the quality of dissolving solution produced.

In all earlier attempts, the effluents from the pits were directly recycled to the process in batches. This disturbed the quality in batches causing cyclic variations which disturbed quality.

A modified scheme was therefore put into operation with a view to bring control and continuity in the recycling operation. The salient features of the modification were:

- Collection of effluents from the pits into a intermediate tank.
- Recycling from the tank to the digestor at controlled rate via a flow control valve.
- Cascading the flow of effluent with the nitric acid flow to digestors to take care of load variations.
- Provision to recycle part of sand washing effluent also to the intermediate tank in case effluent from pits is insufficient to meet water requirement of digestors.

With the implementation of this scheme, we have been successful not only in maintaining continuity of effluent recycle without disturbing process but also in recovering part of the sand wash effluent. The total discontinuous effluent now being generated is around 30 m^3/day against the design value of 240 m^3/day.

CONCLUSION

In this paper we have discussed some of the technical innovations and environmental development done by GNFC based on experience gathered over the period of last eight years of operating nitrophosphate complex. The operating experience of GNFC with its integrated ANP and CAN plants indicates that the quality of rock phosphate is very important when processing with nitric acid for the manufacture of nitrophosphate through Odda process route. It is difficult to get a rock of tailor made specifications as rock is a mineral with many impurities. An in depth knowledge of the effects of various impurities is therefore essential to gain insight into the impact these impurities have on the process. An innovative approach coupled with continuous study and analysis can help to extract the benefits from the various constituents of rock phosphate in order to process economically.

Figure 1

BLOCK DIAGRAM OF ANP / CAN PROCESS

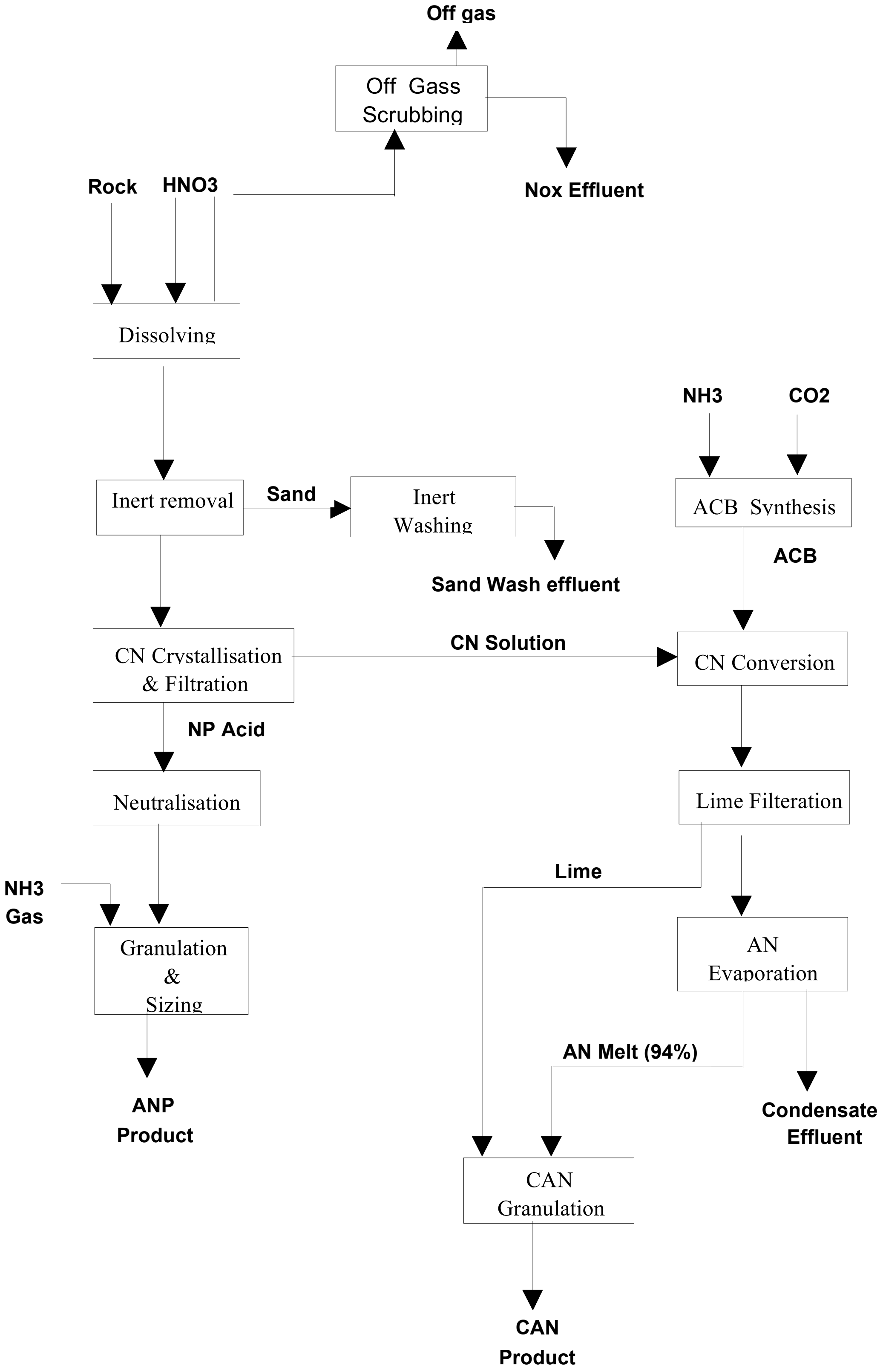


Figure 2

OPERATION OF CNTH FILTER AFTER MODIFICATION

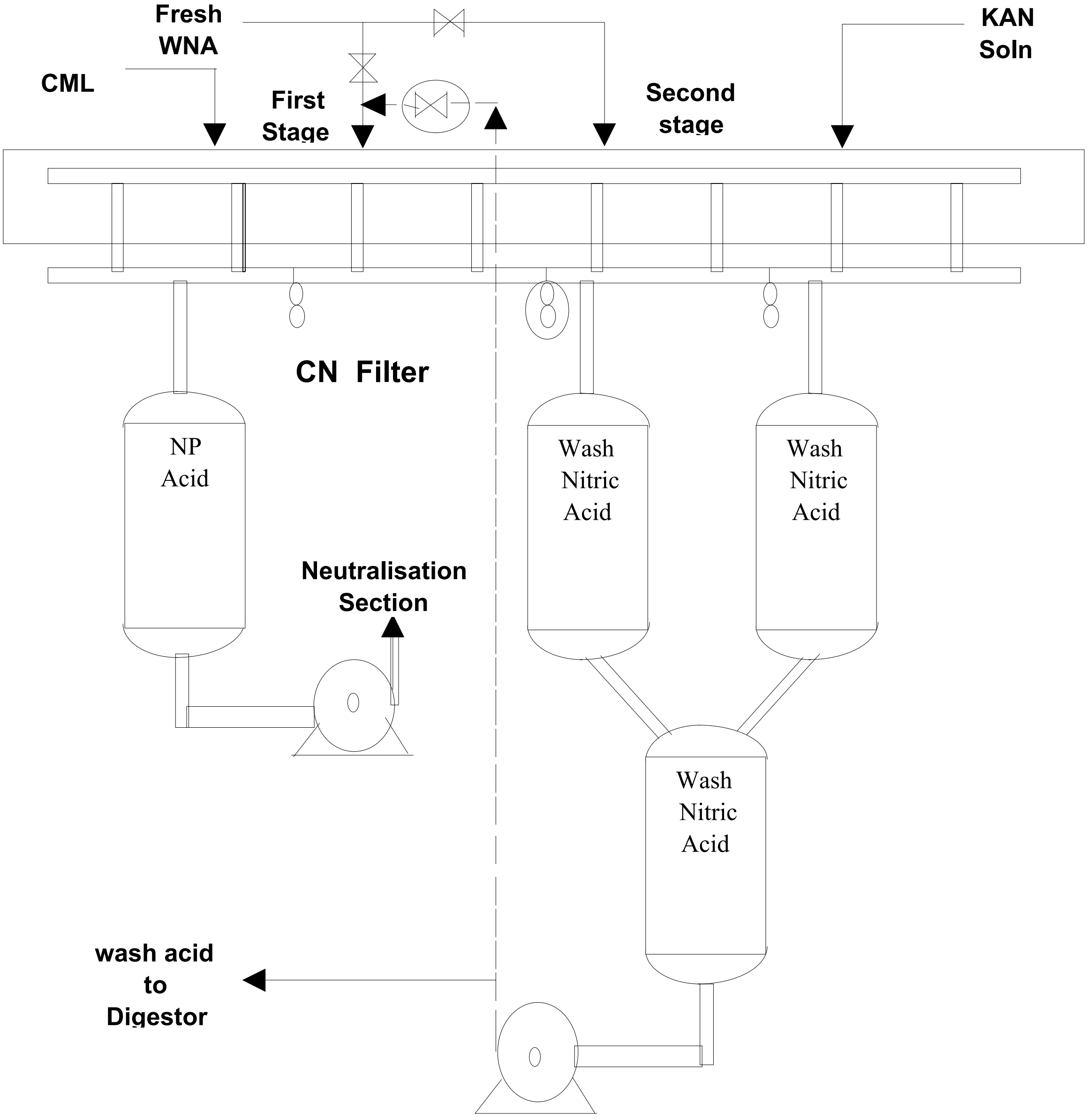


Figure 3

SCHEMATIC DIAGRAM OF BRINE FLOW IN CRYSTALLISERS

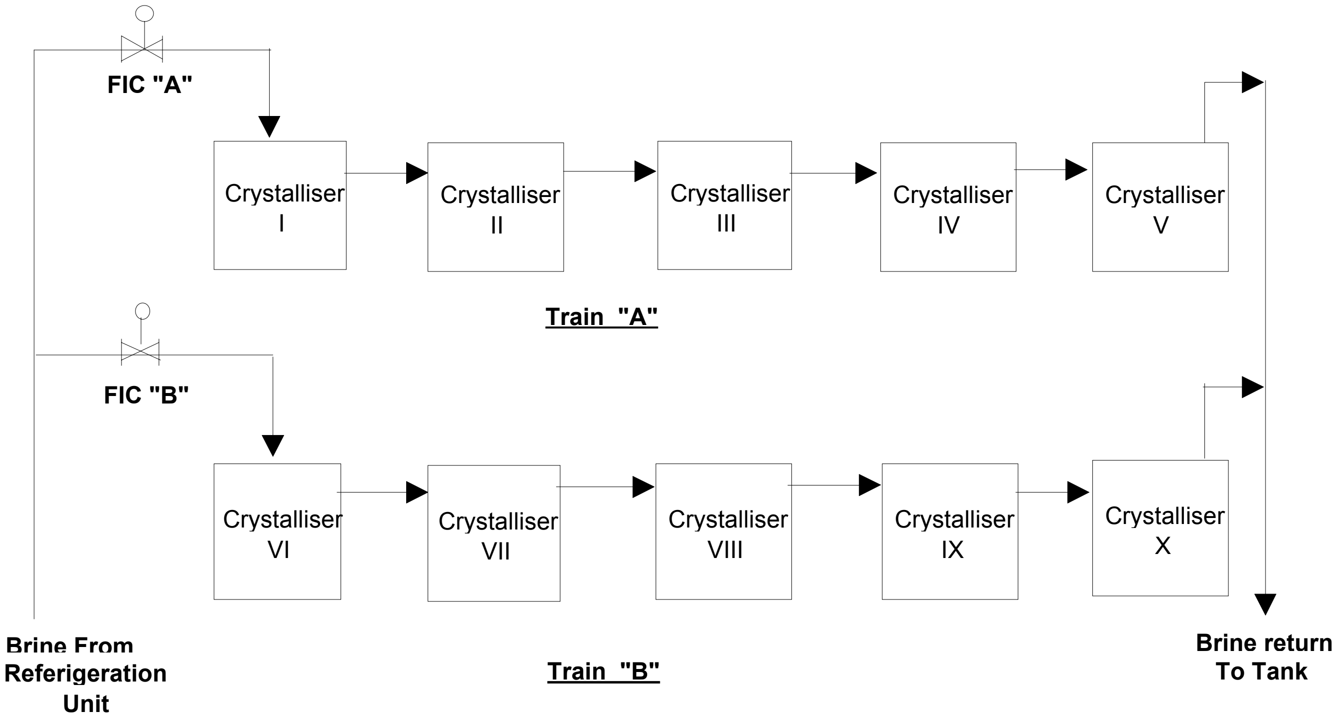
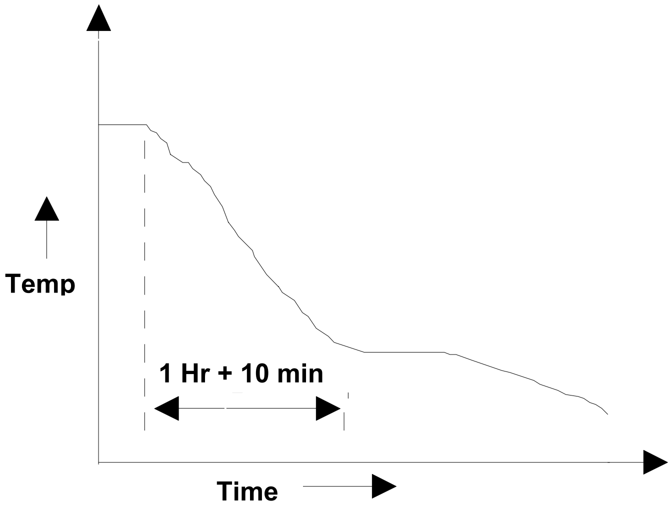


Figure 4

CN CRYSTALLISATION CURVE

(A) BEFORE IMPLEMENTATION OF CHANGE



(B) AFTER IMPLEMENTATION OF CHANGE

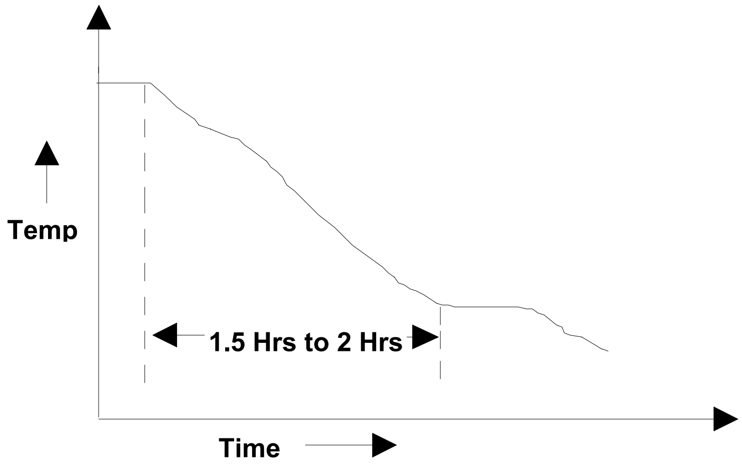


Figure 5

AN SYNTHESIS IN ACB COLUMN