International Fertilizer Industry Association

IFA Technical Conference

Beijing, China
20-23 April 2004

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

FLUORINE RECYCLING: A NEW APPROACH ON EFFLUENT MANAGEMENT IN PHOSPHORIC ACID PLANTS

Arjun Chari*, S. Subbiah**, T.N.V.Satyanarayana***

Traditionally the fluorine evolved during the manufacture of phosphoric acid by acidulation of rock phosphate, is recovered as hydrofluosilicic acid, which is then used to produce downstream products based on their market potential. Many of the plants rely on conventional methods of neutralization and evaporation ponds/stacks, considering the geographical factors of plant location.

This paper addresses an innovative technique to reduce fluorine bearing liquid effluents, that is being implemented at Indo Jordan Chemicals Company Ltd. (IJC), in Jordan, based on know-how from Deutag France and on bench-scale studies carried out at IJC.

A: PREAMBLE

Indo Jordan Chemicals Company Ltd. (IJC), a joint venture company promoted by . Southern Petrochemical Industries Corporation Ltd. (SPIC) - India, . Jordan Phosphate Mines Co. Ltd. (JPMC) - Jordan, and The Arab Investment Company SAA (TAIC) - Saudi Arabia, has established a Phosphoric Acid Complex in the Special Industrial Free Zone in Eshidiya, Jordan.

The Phosphoric acid complex consists of a 2,000 MTPD Sulphuric acid plant, based on Monsanto's Double Conversion and Double Absorption process, a 700 MTPD P2O5 Phosphoric acid plant based on Hydro Agri's single stage Hemihydrate process, and associated utilities and offsites.

IJC commissioned its plants early 1997 and crossed 100% capacity utilisation of its plants for five out of the six years since its commissioning.

Various measures have been taken even at the design stage, as well as during early operation of the plants, to reduce effluent generation at the source and to recycle effluents within the complex.

To further improve on such measures, bench scale studies were conducted to recycle hydrofluosilicic acid recovered in the plant back to the reaction system, based on process know-how obtained from Deutag France. As a result of the positive results of the Bench Scale studies, as well as plant trials, it was decided to implement the recycling scheme on a commercial scale in the plant.

Received 16 February 2004 for presentation at the 2004 IFA Technical Conference, 20-23 April, Beijing, China
* Managing Director, ** Asst. Managing Director (Site), *** Manager (Process Eng.)
E-mail: paamd@ijcshdya.com.jo

This paper describes the development and implementation of the fluorine recycling process in a Hemihydrate phosphoric acid plant, with specific reference to the following.

- Process know how for Fluorine Recycling.
- Bench Scale studies conducted and inferences.
- Plant trials carried out and the results.
- Project implementation.
- Benefits from Fluorine Recycling Process.
- Future prospects for Fluorine Recycling in Phosphoric acid plants.

B: PROCESS KNOW HOW FOR FLUORINE RECYCLING

The (late) Pierre Becker of Deutag France, based on his rich experience in the Phosphate industry, developed the process know-how on recycling of hydrofluosilicic acid in phosphatic fertilizer plants.

During the course of discussions with Mr. Becker on the applicability of the know how to our plant, it was felt that Bench Scale studies needed to be conducted to ascertain the feasibility of the process and to collect data necessary to establish the design criteria for implementation of the system in the plant.

C: BENCH SCALE STUDIES CONDUCTED AND INFERENCES

Based on the process know how inputs from Deutag France, a Bench Scale Unit was set up to examine the feasibility and to conduct process development studies for Fluorine Recycling in a Hemihydrate phosphoric acid plant.

a) Description of the Bench Scale Unit (BSU)

The Bench-scale Unit essentially simulates the Reaction/Filtration system of the IJC plant. The capacity of the Unit is 3 kg/ hr rock. It consists of a set of equipment for fluorine recycling, a battery of three reactors, rock feeding system, a peristaltic pump for recirculation of slurry, along with filtration equipment. The unit is also provided with suitable instrumentation and metering devices, and can be operated continuously. Both Hemi hydrate and Dihydrate process routes can be employed, though the unit has been operated in Hemi hydrate process route only, during our trials. The scheme employed for the Bench Scale Unit is enclosed as **Figure 1.**

b) Details of Tests carried out:

Wet rock phosphate containing 14-18% moisture (70-72 TCP) from two Rock Phosphate mines (Al Abiad and Al Eshidiya) was tested. Since the BSU cannot be used for wet rocks, the rock phosphate was dried and used. Hydrofluosilicic acid with suitable concentration was used. The following trials were carried out.

- Dry Abiad rock (70-72 TCP) alone.
- Dry Abiad rock with FSA (10 % - FSA solution / MTP2O5)
- Dry Abiad rock with FSA (20 % - FSA solution / MTP2O5)
- Dry Eshidiya rock (70-72 TCP) alone.

- Dry Eshidiya rock with FSA (10 % - FSA solution / MTP2O5)
- Dry Eshidiya rock with FSA (20 % - FSA solution / MTP2O5)

During each trial, several filtration tests were carried out and the characteristics of crystals were checked. Additionally, the consumption of rock phosphate and sulphuric acid were measured.

c) Inferences from BSU studies:

Based on the tests, the following inferences could be made.

1. The operating parameters were stable in all the trials conducted, either with or without use of FSA.
2. The shape / type of the hemi crystals (agglomerates) was unaltered whether FSA was used or not during the trials.
3. There was reduction in specific consumption of sulphuric acid by around 5-6 %, and the reduction was proportional to the quantity of FSA added to the system.
4. There was marginal reduction in filtration rate when higher ratio of FSA to rock was used.
5. The suitability of the process for wet rock phosphate could not be established as dry rock was only used in all the trials.

D: PLANT TRIALS CARRIED OUT AND THE RESULTS

Having established the feasibility of recycling fluorine in the Hemihydrate plant on a Bench scale, short plant trials were conducted to study the impact on process parameters and on filtration efficiency in actual plant conditions, as well as to validate and compare the results obtained from the Bench Scale studies.

The following plant trials were conducted, and the plant parameters were optimized based on the data collected from the BSU studies.

a) Trial 1:

This trial was carried out by recycling FSA solution (10 % - FSA solution / MT P2O5). The following is the summary of the observations made:

1. Total quantity of FSA solution used was 30.4 MT and the plant was operated at 60 to 120% of the design capacity. During the trial, plant was operated using 70-72 TCP wet rock phosphate (14-18% moisture) from Eshidiya mines.
2. The plant parameters were normal during the entire period of trial run and the filtration was found to be as good as it was when FSA was not used.
3. There was a marginal reduction in the specific consumption of sulphuric acid.
4. No mechanical problems were experienced during the trial run with FSA.

b) Trial 2:

This plant trial was carried out by increasing the recycling rate of FSA solution (20 % - FSA solution / MT P2O5). The following is the summary of the observations made during this plant trial.

1. Total quantity of FSA solution used was 45.7 MT and the plant was operated at 60 to 120% of the design capacity. During the trial, plant was operated using 70-72 TCP wet rock phosphate (14-18% moisture) from Al Eshidiya mines in the first half and then switched over to 70-72 TCP wet rock phosphate (14-18% moisture) from Al Abiad mines.
2. The plant parameters were normal during the entire period of trial run with increased rate of addition of FSA and the filtration was found to be as good as it was when FSA was not used.
3. There was reduction in the specific consumption of sulphuric acid, which was slightly more than that observed during Trial-1.

E: PROJECT IMPLEMENTATION

Since the results from plant trials also corroborated the test results of the Bench Scale Unit, particularly with respect to stable operation of the plant as well as reduction in specific consumption of sulphuric acid, it was decided to install a permanent system for FSA recycling in the plant, by selection of suitable equipment.

Considering the availability of resources and expertise within IJC, the project is being executed on a non-turnkey basis.

Highlights of the project execution are:

1. The Design Basis for the project was developed jointly by M/s IJC and M/s Deutag France, taking into account the current plant capability.
2. The Basic Engineering Package for the project was prepared by IJC.
3. Detailed Engineering is by JS Associates.
4. Civil and Mechanical Erection works were executed by IJC.

The project is expected to be commissioned by end-April ’04.

F: BENEFITS FROM FLUORINE RECYCLING PROCESS

Based on the Bench Scale studies conducted and short Plant trials carried out, the expected benefits are summarized below.

a) Neutralisation costs:

Traditionally fluorine bearing liquid effluents from Phosphoric acid plant are neutralized with lime as part of effluent treatment. With Fluorine Recycling Process being adopted, the cost of neutralization of effluents gets reduced substantially, depending on the extent of recycling.

The estimated cost savings from the neutralization of effluents with lime for a typical 700 MT P2O5 / day Hemihydrate plant is around USD 850,000 per annum, based on the cost of lime at USD 90 / MT.

b) Reduction in Effluent Quantity:

Since substantial quantity of fluorine is recycled, there is net reduction in fluorine bearing effluents. Though the extent of actual reduction in effluent quantity depends on the water balance in PA plant, around 25-40% reduction in net effluent is expected when fluorine recycling process is implemented. This would in turn reduce the consumption of fresh water for the complex, depending on the total water balance.

c) Savings in Sulphuric acid:

Incidentally when Fluorine Recycling process is used, the specific consumption of sulphuric acid gets marginally reduced, which is expected to reduce the cost of production by USD 1.5 - 2.5 per MT P2O5.

G: FUTURE PROSPECTS FOR FLUORINE RECYCLING IN PHOSPHORIC ACID PLANTS

With limited market potential for economical use of recovered fluorine from phosphoric acid plants, most of the plants rely on conventional neutralization and/or recycling schemes based on geographical conditions to meet environmental regulations. Hence, Phosphoric acid producers would welcome technology for cost effective treatment of fluorine bearing effluents.

The Fluorine Recycling technology does not envisage production of another product to be marketed, but instead it requires recycling within the Phosphoric acid plant, which, incidentally, reduces the specific consumption of sulphuric acid. This important aspect makes the Fluorine Recycling technology very attractive for Phosphoric acid producers.

Though the Fluorine Recycling technology is now being implemented in a hemihydrate Phosphoric acid plant at IJC, there is no reason why it should not work in dihydrate plants also. However, Bench Scale tests need to be carried out to obtain data regarding process parameters, and the distribution ratio of fluorine in reaction stage and the water balance in the plant needs to be reviewed, prior to adopting the Fluorine Recycling technology in any Phosphoric acid plant.

H: CONCLUSION

On the basis of the results obtained so far, it can be stated that the Fluorine Recycling is a promising technology for cost effective effluent management in Phosphoric Acid plants, vis-a-vis the traditional neutralization of effluents.

Incidentally, Fluorine Recycling also reduces the consumption of Sulphuric acid for production of Phosphoric acid.

It is hoped that the Fluorine Recycling technology would eventually emerge as the state of the art technology in the future for effluent management in Phosphoric Acid Plants.

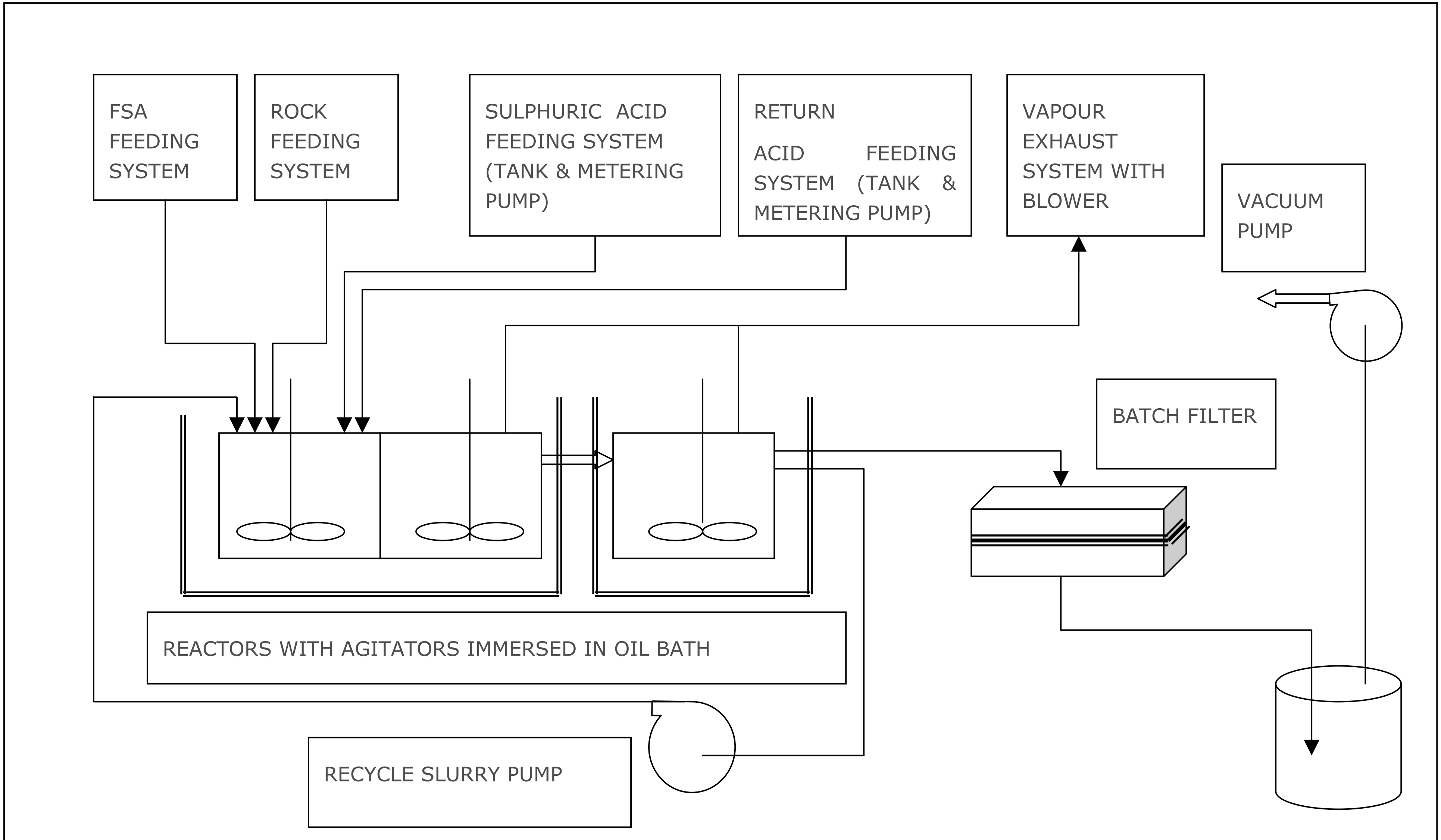

FIGURE - 1 SCHEMATIC DIAGRAM FOR BENCH SCALE UNIT