RECENT DEVELOPMENTS

IN

PHOSPHATE FERTILIZER TECHNOLOGY

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1. INTRODUCTION

Recent developments in the phosphate fertilizer industry are placing new expectations and focus on scrubber design. The developments in regards to decreasing emissions and the integration of multiple scrubbing functions (i.e. dust, fluorine, and ammonia control) into a single installation, have created new challenges for the designers, fabricators, and users of these pollution control technologies.

This paper will discuss recent experiences at fertilizer plants in South Korea. This country was chosen due to a change in emissions regulations, specifically fluorides, which led to considerable improvement in the desired scrubber performance. Project-specific cases will be examined, with emphasis placed on several case histories that have established new standards in recent years.

In the cases to be considered horizontal cross-flow scrubbers were used. A horizontal cross-flow scrubber is a very flexible type of scrubber that typically includes conditioning spray sections followed by mesh packing sections. These scrubbers are uniquely designed to clean gases at varying concentrations and under severe conditions (FIGURE 1.)

Failure or success in meeting the standards for air quality depends on a combination of factors. Of those, selection of a scrubber technology is the first and foremost factor. A design/engineering company often considers selection of a scrubber vendor based on;

- broad knowledge/experience
- initial cost of the unit and net operating cost
- minimum financial liability from negative variance in performance guarantee or contract

However, the user ultimately remains responsible both legally and financially to correct performance problems prior to operating the plant on a regular basis.

This paper deals with the use of the horizontal cross-flow scrubber with mesh pads for mass transfer and phase separation. Information on mesh and other aspects regarding its use have been published previously. (References:1, 2, 3, 4.)

2. POLLUTANTS

In agrochemical industries, scrubbers are designed for absorption of HF, SiF_4, NH_3, SO_2, etc. in scrubber inlet air with an aqueous solution associated with chemical reaction involved in process and for the separation of solid particulate.

The physical characteristics such as particle size and phase distribution of the contaminants vary widely. This in turn increases the degree of difficulty in controlling them. The problem is further compounded by changes in the plant operation --- debottlenecking, product change, etc.

TABLE 1

TYPES OF CONTAMINANTS IN PHOSPHATIC FERTILIZER PRODUCTION

CONTAMINANT	**PHYSICAL DESCRIPTION**
HF & SiF_4 Vapor	Gaseous
HF & H_2 SiF_6 Aerosols	1µ – 6 µ fog
HF & H_2 SiF_6 & Pond Water Entrainment	50 µ – 500 µ drops
Rock & Fertilizer dust	10 µ – 100 µ particulate matter Occasionally also 1µ - 10 µ particulates
Ammonium-Fluoride/Bi-Fluoride Aerosols	Submicron particulates or liquid

The above contaminants must be removed by the correct combination of absorption and/or phase separation (mist elimination, aerosol separation). Ideally the control technology should be robust or relatively insensitive to scrubber input conditions.

A clear understanding of the consequences of possible physical and chemical changes and/or interactions within the process system is essential in designing an appropriate pollution solution. For example:

- Aerosol formation by the gas phase reaction of basic ammonia and acidic gases, eg. HF, HCl, etc. commonly yields very fine solid particulate ammonium salts – fluorides, chlorides, etc. These are known as reaction aerosols. (It should be noted that while ammonia or fluoride scrubbing is relatively simple, the control of the reaction aerosol ammonium fluoride is harder to achieve.)

- Fog is formed by condensation aerosols of water vapor and fluoride/chloride compound vapors which is not absorbed in a conventional counter-flow system.

Further information on aerosol separation can be obtained by contacting the author.

Far too often, it is assumed that different contaminants and/or different phases can be treated similarly. For example, there is sometimes a tendency to rely on simple absorption calculations in the design phase of a project, with insufficient regard paid to other factors. Of course, there is a hidden trap in focusing too narrowly on HTU calculations: WHAT IF NOT ALL THE POLLUTANT IS AN ABSORBABLE VAPOR? This is not a trivial question; one can document hundreds of cases in which gas phase absorption analysis was used as a basis for solving a problem that did not involve solely a gaseous component. Typical examples are when the pollutant is present in the gas in association with solid particulates, sub-micron chemical aerosols, and fog. While this paper does not deal with these issues in depth, they are variables of paramount importance in the process and mechanical design of a system. For example, fluoride from in a single gas stream of a diammonium phosphate plant has been found to be present as: HF gas, SiF_4 gas, ammonia + fluorine compounds (as sub-micron aerosols), fogs of HF + H_2SiF_6 in solution, pond water irrigation entrainment, and in conjunction with process particulates. Proper process design will prevent the formation of the sub-micron aerosols. A design that does not account for all three of the other forms of fluoride is incomplete.

3. DESIGN CONSIDERATIONS

Appropriately designed systems will allow for a wide realm of various mechanical and chemical considerations.

I. Simple Mechanics

Given the wide range of mechanical issues to be encountered in the operation and maintenance of the scrubber, it is at the design stage that experienced engineers will make the scrubber as economical as possible.

The cross section of the appropriate vessel is determined first by the gas flow. Then the width is established usually in 1.8m (6 feet) increments to make optimum use of the standard Kimre™ mesh width. The allowable height is a function of the gas velocity and the liquid load of the packing stages. To prevent re-entrainment of the scrubber liquid, height of the packing is typically limited to 3m (10 feet.) If site requirements or fabrication economics dictate a taller scrubber cross section, an intermediate drain can be designed into the frames supporting the mesh packing (FIGURE 2.)

The vessel length is determined by the number of stages, the scrubber liquid distribution system and appropriate inlet and outlet transitions. An important consideration in the vessel length is the possible need for additional absorption efficiency at a later date. It may be advisable to build the scrubber vessel long enough to accommodate additional absorption stages, remembering each additional stage can provide 3 to 4.5 transfer units. Typical vessel sizes require one meter length per stage (Figure 1.)

The first precaution is the use of discrete stages of packing in slide-in/slide-out frames. The use of multiple stages also has the advantage that if one stage is removed or otherwise put out of service, the scrubber will still remove a very high proportion of contaminants. Clearance must also be allowed for frame removal; this is typically accomplished by bringing a crane into position.

While a horizontal scrubber is not as sensitive to liquid distribution as a counterflow scrubber, liquid distribution is still an important consideration. Poor distribution can cause channeling and/or allow premature plugging of the mesh packing. In the typical corrosive, pluggage-prone situation, spray systems need to allow easy, safe removal of nozzle lances for cleaning and/or replacement. Since the typical scrubber liquid causes both chemical and mechanical wear on the nozzles in addition to plugging, quick-change nozzle lances are strongly recommended.

At typical pressure drops (1 in W.C.) bypass of gas flow at the frame edge is easily dealt with by sliding the frame into channels. The force of the gas flow is sufficient to force the frame and packing against the downstream lip of the channel thus creating a seal. Proper frame and channel construction is critical in preventing bypass, including enough “play” to allow a frame of plugged packing to be removed (FIGURE 3.)

Bypass between the scrubber mesh and frame is best handled by letting the packing manufacturer supply the completed frame and packing assembly. Depending on the scrubber design requirements, it may be necessary to separate the sumps by stage and provide individual distribution pumps. This can provide stagewise counterflow whereby the most heavily contaminated gas contacts the scrubber liquid with the highest contaminant concentration.

Spray design is best done by a reputable nozzle supplier. An essential point is 100% or greater coverage to avoid channeling. The mesh packing supplier requires full-cone nozzles with less than 90 degree angle to provide adequate penetration into the packing.

Figure 4 shows the appropriate design inlet and outlet transitions needed to give gas distribution across the cross section of the scrubber. In revamping existing equipment, the need for coordination between the equipment owner and the mesh packing supplier is critical due to pre-existing conditions.

All scrubber drains must be given adequate barometric traps or run to a sump. Failure to do this causes bypass through drains or allows the entry of ambient air. The drains need to be easily accessible and cleanable.

II. The Right Chemistry:

"If you know the temperatures and chemistry of the constituents, it is simple" (Reference 5.)

Increasingly stringent environmental controls have so far caused increasingly conservative scrubber designs. The situation is aggravated by the lack of reliable vapor pressure data. This situation has been recognized by the industry for many years and a data acquisition program to acquire better data is in the discussion stage. For the immediate future however, scrubber design will continue to be conservative.

An additional reason for conservative design is inlet process water fluctuations. Variations in composition and temperature of the scrubber liquid supply (typically gypsum pond water) are often times seasonal or due to alterations in pond operation.

The existence of solids, whether from precipitation in the scrubber or from the gypsum pond, may require stagewise recirculation with the requisite separate recirculation sump, solids filter, and spray system for each stage.

The last source of process disturbance to be discussed is upstream changes in the fertilizer plant itself, as relates to fertilizer product specifications. Even though these are deliberately planned disturbances, the resulting shifts in off-gas composition are not easily measured or predicted. Again, one is forced to apply conservative designs to level out the disturbances without exceeding the emissions limits. In the mixed fertilizer plants the need to achieve control over several outlet variables becomes even more challenging.

Pluggage is particularly a problem in fertilizer operations and must be provided for in the design. Pluggage minimization and control of the consequences of pluggage is actually one of the primary design factors in many scrubber operations. Pluggage can be caused by a variety of reasons both mechanical and chemical. Typical examples are:

- Failure of the irrigation system yielding a formidable cement-like solid typical of phosphoric acid plants.

- Reactive gases, such as silica on tetrafluoride reacting with water to precipitate silica. This is typical of single super phosphate plants.

- Reaction of gaseous components with components in the water forming, for example, calcium-ammonium fluosilicate precipitates. This is a known problem in Florida DAP Plant operations.

4. BENEFITS OF SXF™ DESIGNED SCRUBBERS

The main impetus for the improved scrubber performance in Korea was the new limit of 3 ppmv fluorine in the early '90's'. Since this value is only slightly above typical gypsum pond water equilibrium values, increased scrubber efficiency was required. To meet this stringent requirement Kimre proposed its proven SXF™ Semi-Crossflow scrubber technology.

Semi-Crossflow or SXF™ units are usually a combined conditioning spray (upstream) and mesh (downstream) sections that work well for agrochemical processes such as phosphoric acid/fertilizer and pesticide, incinerators, emergency vents, etc. (FIGURE 1.)

Semi-crossflow refers to scrubbers in which the liquid (usually aqueous solutions or slurries) is sprayed concurrently with the gas onto the upstream side of the Kimre KON-TANE™ Tower Packing stages. (Occasionally the spray is on the downstream side, as well.) The gas flow is horizontal. The liquid runs down the pad crossing the gas flow and discharges at the bottom.

Typically, an upstream conditioning spray section cools and saturates the gas. This design feature has become standard for most applications. The upstream conditioning sprays significantly improve the scrubbing efficiency of the downstream packing stages by saturating the gas and reducing the solids loading within the gas stream prior to making contact with the downstream stages.

The horizontal crossflow scrubber provides easy access to the scrubber internals. It is more readily available for repair and start-up than any vertical tower. The crossflow mesh unit is more easily adaptable for changes in design/operating conditions, if a situation arises (FIGURE 5.)

KON-TANE™ tower packing in a six-layer configuration, as used in SXF™ scrubbers has been found experimentally to provide 3 to 4.5 NTU's for both mass and heat transfer for a wide range of flow conditions in many applications. Three NTU's is used as a design value (REFERENCE 6.)

KON-TANE™ tower packing is typically incorporated into cassettes (FIGURE 6.) The cassette and vessel are designed so that they fit together in a manner that allows the cassette to be easily removed during operation or for maintenance. A variety of designs are available for different applications. Typical fertilizer designs are the Pants Hanger™ cassettes. Problems of by-passing within the cassette and around the cassette, although complex, have been completely solved to provide a very reliable, predictable operation. Cassettes holding modular mesh sections are typically identical to each other. This provides for greater system flexibility should it be necessary to add or remove the mesh media or stages afterwards for either increased production rate or meeting a more stringent emission levels.

Properly designed SXF™ scrubbers achieve higher scrubber efficiency at the same power consumption of other technologies. Stage-wise absorption improves performance. For example, if a Venturi cyclonic scrubber is designed for 95% efficiency, an SXF™ scrubber can achieve fluorine removal of 99.9% and higher at the same power consumption. The above claim is based on the design and implementation of many scrubber systems in Central Florida and worldwide that meet current fluoride emission levels set by regulatory authorities.

The ability of an SXF™ scrubber to generate highly concentrated waste with minimal recycle is unsurpassed. Its ability to generate concentrated (FSA) hydrofluorosilicic acid as in single super phosphate plants, is well documented and known.

SXF™ scrubbers will require more transfer units than counter-flow scrubbers if the liquid and gas rates are the same. However, the difference is insignificant compared to other uncertainties given that either the counter-flow tower or the cross-flow scrubber can be designed for any number of transfer units. NTU values of more than 10 and scrubber efficiencies of more than 99.9%+ had already been obtained from cross-flow mesh scrubbers in phosphoric acid/fertilizer processes using KON-TANE™ mesh in Florida, Louisiana, Wyoming, North Carolina, Idaho, China, Australia, New Zealand, Philippines, France and elsewhere to meet applicable air emissions standards.

5. RECENT EXPERIENCES IN PHOSHORIC ACID AND NPK

Namhae Chemical Phosphoric-Acid

The Namhae Chemical Phosphoric Acid Plant Project in Yosu South Korea involved a Kimre retrofit to replace dumped packing in the fluorine fume scrubber. The design guarantee for this system was 3ppm volume from an inlet of 9% fluorine in the gaseous phase. Three KON-TANE™ tower packing stages followed by a B-GON™ mist eliminator were installed in the existing vessel following modifications. The existing upstream spray section was utilized as a conditioning stage to pretreat the gas coming from the digestor. Due to the stringent design requirements, the final stage recycled a separate and cleaner liquid with fresh water make-up. This required a separate sump, as well as the addition of an interstage dam to prevent carryover of liquid between the second and third stage. Namhae originally purchased a spare stage (two frames) which are interchangeable between stages for reduced maintenance downtime (FIGURE 7.) This installation has been in service for four years and continues to exceed all emissions requirements.

Namhae Chemical NPK

Following the success of the Phosphoric Acid Project, the SXF™ design was again the chosen technology for two NPK units at Namhae Chemical in Yosu.. Again the design was guaranteed to meet 3 ppm fluorine. The off gas flowrate and space availability required Pants Hanger™ frames in excess of twenty feet in height (Figure 2.) Kimre supplied modular frames that featured connecting clips that allowed two frames to be stacked one on top of the other. Each pair of stacked frames utilized interconnected internal drains, thus preventing flooding in the lower regions of the media due to an excessive volume of liquid drainage from the upper regions of the packing stage. Clipped together, these frames are installed and removed two at a time via a crane hoist. Limited space requirements dictated inlet and outlet requirements that differ from that typically recommended (FIGURE 8.)

This installation has performed exceptionally well for several years, recording fluorine emissions (1.4 ppm) less than half the guaranteed level (3 ppm.) The performance of this system was (and to the author's knowledge, is currently) unmatched by any other similar application throughout the world.

The user recently made reactor modifications on one of these lines. The inclusion of a pipe reactor has increased ammonia concentration. The additional ammonia in the presence of MAP causes a MAP slurry previously not encountered in this installation. The first stage of KON-TANE™ tower packing required cleaning every three to four days (down from three to four weeks). The solution was the installation of additional upstream conditioning sprays as well as an additional set of sprays on the downstream side of the first KON-TANE™ stage. Limited space availability within the vessel necessitated that the conditioning sprays be installed in the inlet duct. Inclusion of the duct sprays has solved the problem by removing a significant amount of the particulate prior to making contact with the media while simultaneously bringing the gas stream closer to saturation which improves the mass transfer within the scrubbing stages. Conditioning sprays have become a standard design feature on similar installations in recent years..

Most Recent NPK Installation

A more recent project involved another NPK plant in South Korea. This project would prove to be an extremely aggressive undertaking. The plant is designed to supply up to thirty different phosphatic grades to target the relatively short seasons of the domestic small plot fertilizer market. Production runs would be fairly short. Process fluctuations would be extreme. Planned shutdowns were to be minimal. And of course the user required a fairly stringent outlet guarantee:

Pollutant	Specified Inlet	Guarantee
Dust	300 to 1000 mg/Am^3 (3000 mg/Am^3 Max)	90% removal
Fluorine (all forms)	50 to 100 mg/Am^3 (200 mg/Am^3 Max)	90% removal
Ammonia (all forms)	50 to 300 mg/Am^3 (1000 mg/Am^3 Max)	85% removal

Further, the client required a guaranteed limit on waste liquid discharge of 10 m^3/hr. This additional specification understandably increases the constraints under which any type of scrubbing system operates.

Kimre proposed a system to meet or exceed all of the specified design requirements. Kimre's proposed system utilized all of the features discussed previously, including conditioning sprays, Pants Hanger™ frames and stage-wise recirculation of scrubbing liquid. The relatively low liquid discharge guarantee is met by utilizing counterflow stage-wise recirculation of scrubbing liquid. This optimizes mass transfer driving forces with limited availability of scrubbing liquid by contacting the most concentrated liquid streams with the most polluted gas, and the clean liquid streams with the least polluted gas. Kimre's offer was contingent upon vessel drawings approval and vessel construction according to specifications. Several days following order acceptance, it was revealed that vessel fabrication was already 80% complete and the original modifications would not be possible. With startup less than three months away, Kimre was able to alter its design. The system with the new modifications was delivered early, showing the flexibility of the SXF™.

Although results were not available at press time, Kimre remains confident that this system can nevertheless meet emissions requirements in regards to dust, fluorine and ammonia.

This project underscores the importance of appropriate coordination in the design parameters of any installation.

6. CONCLUSIONS

Horizontal crossflow scrubbers are amenable to aggressive environments with varying compositions in inlet gas and offer flexibility in design and application and therefore solve environmental control problems in agrochemical industries. Extremely stringent emissions limits have been achieved on a regular and reliable basis.

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