Fluorine from phosphate mining waste

Phosphoric acid by-products could be a new source of hydrogen fluoride, as James Eldridge of Kimre Inc. explains

PHOSPHORUS IS A vital nutrient. Every living organism – plant or animal, single celled to vertebrate – requires phosphorus. Element number 15 in the Periodic Table, phosphorus is a basic component in the helical structure of DNA. Phosphorus is also utilised in energy transport in all living matter. Additionally, in vertebrates phosphorus is critical for proper bone and teeth formation.

Phosphorus is found in living organisms as phosphate (PO$_4^{3-}$) ion associated with other chemical species. As a fertiliser, the only significant source is phosphate-bearing minerals, which must be mined and processed into other chemical species that world agriculture can utilise.

The phosphate industry produces a number of by-products, including traces of hydrogen fluoride (HF) gas that must be collected in gas scrubbers at extremely high efficiency to prevent environmental harm. The purpose of this paper is to give a brief explanation of how an untraditional and innovative cross flow scrubber design can achieve this as well as helping the phosphate industry recycle its scrubbers’ liquid waste stream into a high value product.

Phosphate by-products

Phosphate ores are found in both igneous and sedimentary type rocks in two primary forms:

**Fluorapatite** (igneous formations):

$\text{Ca}_10(\text{PO}_4)_6(\text{F}, \text{OH})_2$

**Francolite** (sedimentary formations):

$\text{Ca}_10(\text{PO}_4)_6(\text{CO}_3)_x(\text{F}, \text{OH})_{2-x}$

Note that the element F, fluorine, is present in both types of ores. All phosphate ores therefore contain some level of fluorine. Additionally all ores contain some level of silicon. Note the compositional and elemental analyses (partial) of example ores from various locations around the world (Figure 1).

As a result of the compositions noted in Figure 1, all phosphate ore processing produces some amount of fluorine as a by-product; primarily HF. Further, the presence of silicon assures that silicon tetrafluoride (SiF$_4$) is also a by-product.

At normal conditions these species are both gases, but both are also readily water soluble. HF dissolves to form hydrofluoric acid. When SiF$_4$ dissolves in the presence of HF a new species, $\text{H}_2\text{SiF}_6$, fluosilicic acid* or FSA is formed. In typical air pollution control unit operations, known as packed bed wet scrubbers, HF and SiF$_4$ are both absorbed into the scrubbing liquid. As a result, a dilute solution of fluosilicic acid quickly forms and this is the scrubbing liquor used during normal steady state operation of the scrubber.

Another by-product is gypsum (CaSO$_4$), or so-called phosphogypsum. This material is the result of process steps where concentrated (98%) sulphuric acid is used to convert phosphate rock into phosphoric acid. The mining district of central Florida is dotted with huge gypstacks (Figure 2) along with associated holding and cooling ponds, used to store water that decants from the gypsum slurry and to process water (such as FSA water) from scrubbers.

As a result, the Florida phosphate industry has several chronic problems of what to do with its by-products. Some of the water in the ponds is recycled back into the fertiliser production process, but a large volume of water acidified with fluorine from phosphate mining waste

*Also sometimes fluorosilicic acid, the spelling of the name as used in this paper, fluosillic acid, is per Webster’s New Universal Unabridged Dictionary, 1992. Note references 4 and 5 both use the alternate spelling.

**Figure 1: Examples of phosphate ores**

<table>
<thead>
<tr>
<th></th>
<th>Russia*</th>
<th>South Africa*</th>
<th>Morocco**</th>
<th>Florida**</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition</strong> (% weight)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>38.9</td>
<td>36.8</td>
<td>33.4</td>
<td>34.3</td>
</tr>
<tr>
<td>CaO</td>
<td>50.5</td>
<td>52.1</td>
<td>50.6</td>
<td>49.8</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.1</td>
<td>2.6</td>
<td>1.9</td>
<td>3.7</td>
</tr>
<tr>
<td>F</td>
<td>3.3</td>
<td>2.2</td>
<td>4.0</td>
<td>3.9</td>
</tr>
<tr>
<td><strong>Trace Elements (ppm)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U$_2$O$_8$</td>
<td>11</td>
<td>134</td>
<td>185</td>
<td>101</td>
</tr>
<tr>
<td>As</td>
<td>10</td>
<td>13</td>
<td>13</td>
<td>11</td>
</tr>
<tr>
<td>Cd</td>
<td>1.2</td>
<td>1.3</td>
<td>1.5</td>
<td>9</td>
</tr>
<tr>
<td>Hg</td>
<td>33</td>
<td>0.1</td>
<td>0.1</td>
<td>0.02</td>
</tr>
</tbody>
</table>

* Iigneous Type Deposits  ** Sedimentary Type Deposits
FSA must be disposed of by other means. The present best available method the industry has to move its FSA water is as a fluoridation additive for potable water supplies. Although EPA approved this use of FSA, it has its opponents – it is understandable that many people view a substance that is the product of an air pollution control device as being an undesirable drinking water additive.

The fact that when so used FSA has a minimum dilution factor of approximately 280,000 times has little impact on those who oppose this use of FSA. And use as a drinking water additive is also of only limited utility to the phosphate fertilizer industry. Only a small fraction of the FSA produced by the industry in Florida can be moved in this way and the price received for the FSA is little more than a token payment.

HF recovery

Although viewed as a waste product in the phosphate industry, HF as hydrofluoric acid is the highest value product that the fluorspar industry produces. Fluorspar (CaF₂) is a widely dispersed mineral that is mined as the primary source of HF.

The highest industrial grade (and hence the most valuable form of fluorspar) is known as acid grade, which is used to produce HF. The acid so produced is used to make fluorinated polymers such as Teflon and Kynar. It is also used in the pharmaceutical industry, as well as other products such as aluminium fluoride (AlF₃).

HF is readily recovered from FSA. Therefore, not only could the Florida phosphate industry be able to move its FSA, when the industry drained its holding ponds it would also be a money maker for the trade. Worldwide it is estimated that the phosphate industry produces 2.6m. tpa of FSA (on a 100% basis). From this FSA a maximum of 1.7m. tpa of HF (again, 100% basis or anhydrous) could be recovered.

Several methods of HF recovery from FSA have been proposed. One such scheme is cyclical and therefore almost self-regenerating. Kvaerner Process Technology of Switzerland has successfully commercialised this process.

The basic cycle is outlined in Figure 3. Note three inputs into the cycle are FSA, SiF₄, and concentrated sulphuric acid. The three outputs from the cycle are solid SiO₂, 70% strength sulphuric acid and anhydrous HF gas. The HF, as previously noted, is a high value product that can be sold into numerous industries. Silicon dioxide is a solid and is, basically, fine sand. It is not hazardous and can easily be sold, for example, as aggregate, fill for highway and other construction projects which would represent further revenue to the industry.

The initial capital expense to build a plant to recover HF from FSA plant is high. The most optimal situation for such a plant would be to have a customer close at hand for the HF produced – such as an aluminium plant that had a large AlF₃ requirement.

Lastly, diluted sulphuric acid is also discharged from the cycle. This is the most problematic of the three species so formed in the process. As previously mentioned, the phosphate industry uses sulphuric acid to process phosphate ore into phosphoric acid, which is then converted into value added fertilizer products.

The industry does have a need for sulphuric acid, however this need is for concentrated acid, not 70% strength, eg. diluted, sulphuric acid. As a result the water balance of the process is critical to the commercial viability of the enterprise. Too much water means that the recovered sulphuric acid will be too dilute for the industry to accept. In this situation the industry would essentially be back into the present status of having very limited outlets for FSA water.

The figure noted for the strength of the sulphuric acid discharged (70%) is an estimate. The actual strength of the acid will depend upon the water balance at a given site. Acid at 70% is mentioned because it has proven to be practical – and also tolerable in some instances – in the phosphate industry.

It is very important to note, however, that the more concentrated the discharged sulphuric acid is, the better. 75% strength would be a significant improvement versus 70%, and 80% strength even better. The closer the discharged sulphuric acid can be to the ideal target of concentrated, 98% strength, the less cost must be borne by the industry to recycle the acid into the fertilizer producing process.

Semi cross-flow scrubbing

Kimre, Inc. of Miami, Florida, has been...
supplying KON-TANE scrubber packing and mist capture B-GON pads to the Florida phosphate industry for over 35 years. These media allow for a unique cross-flow design versus more traditional, vertical counter-current wet scrubber. The SXF semi-cross flow scrubber achieves numerous advantages without loss of efficiency versus conventional scrubber designs:

1) Much lower height versus vertical, counter flow scrubber;
2) Easy mounting of pumps, valves, and controls at ground level;
3) Easy access to the above for normal operation and maintenance;
4) KON-TANE and B-GON media are easily mounted into cassettes that allow for on-the-run maintenance of the scrubber;
5) Very easy to accommodate multiple stages – quite possibly with multiple chemistries – in a single vessel;
6) The sumps of the multiple stages can be joint, cascading or a combination;
7) Much wider range of L/G ratios versus a vertical tower, including extremely low L/G.

In the example given the sumps of the several stages are all independent. But, as previously mentioned, the sumps can also be made cascading. Note that as the gas being scrubbed of HF at a phosphate facility passes the scrubber horizontally, left to right in the example, the collected liquor in each sump can be directed in the opposite direction, right to left or counter-current to the air flow.

As a result the FSA solution collected in the first stage sump can be concentrated well beyond what is possible if the scrubber was based upon a traditional, vertical packed tower. Also, the variability of L/G ratio, as well as the ability to use a very low L/G ratio, further allows for concentration of the FSA solution in the first stage sump.

As a result, the bleed (or blowdown) from the first stage can be controlled to have FSA concentration 23% and higher by mass. This compares very favourably to the less than 20% FSA that normally is

Please note the schematic presentation of a SXF type scrubber (Figure 4) has multiple functions. These may or may not be used, in any combination, in scrubbing projects as needed. In the design, air flows into the horizontal vessel and is humidified by passing co-current water sprays. The air being treated then passes stages of KON-TANE where one or more scrubbing goals can be accomplished with very high efficiency. Also note that in this example cooling has been added as an additional process function. As with the initial humidification, scrubbing liquor is sprayed co-currently onto the face of each stage. Then, in this example, two stages of B-GON mist capture are shown.

**Multiple sump design options**

Of particular interest to this discussion is the arrangement of the various sumps.

![Figure 4: Multi-function SXF semi-cross flow scrubber design](image)

![Figure 5: Kimre media cassettes](image)
the blowdown solution strength from the single sump of a vertical scrubber.

And as previously explained the more concentrated the FSA solution the better in the HF reclamation cycle process, as the dilution factor of discharged sulfuric acid will be reduced as a result.

Maintenance

Maintenance of an SXF scrubber is not difficult and the unique design features of such a scrubber can offer additional benefits to the operators. This is because the KON-TANE and B-GON media can be readily mounted in easy to handle cassettes. By mounting the media in a cassette, handling of the media in field conditions – both to install as well as to remove – is not difficult.

It is also practical to pull a media cassette as the scrubber operates. Kimre has several installations of SXF scrubbers around the world where this type of maintenance procedure is routinely performed. The cassette is pulled for whatever reason – inspected, or cleaned if needed – and reinstalled or replaced with a spare cassette all within the span of a few minutes. The scrubber does not shut down so no interruption of production is required. Air pollution regulations are not violated as the remaining operating stages do extra scrubbing duty for a few minutes.

Case studies

In South Korea, the Namhae Chemical Corp. in South Korea has a SXF design based cross-flow scrubber. All pumps and valves are readily accessible as they are mounted at ground level. The manager of manufacturing at Namhae Chemical, Mr. Noh-Jo Park, reports that in the >10 years that the scrubber has been operating that there have been no maintenance problems.

KON-TANE media cassettes are pulled for inspection on the run or during shutdown, per the operator’s preference. No special cleaning or other maintenance has been required. Pressure drop has been steady across the scrubber during its operational history.

In Saudi Arabia, Ma’aden’s phosphoric acid plant utilises an SXF cross-flow design which also allows for modular construction. This is noted in Figure 6, which shows a 150,000 Nm3/hr scrubber that was manufactured in Florida for shipment to a greenfield phosphoric acid plant in Saudi Arabia.

In Figure 6, showing the main body of the scrubber, note the four top doors for the four stages in the vessel. Three stages are for KON-TANE scrubbing and the last stage for B-GON mist elimination. The media cassettes were fabricated in Florida as well and installed in the scrubber body module, seen here, prior to shipment to Saudi Arabia. The transport of the scrubber body in several modular pieces as deck cargo was practical and cost effective. After arrival in Saudi Arabia assembly of the scrubber was readily accomplished by placing the various modules in their proper pre-constructed places at the acid plant.

Summary

Recovery of HF from FSA solution has proven to be feasible, both technically and if local conditions are economically favourable as well. Using Kimre’s SXF semi-cross flow scrubber technology has numerous operational benefits – including producing a concentrated stream of FSA to use in the recovery process. This allows for improvement of the economics of the project further owing to better control of dilution factor of the sulphuric acid solution produced in the HF recovery from FSA cycle.

Contributor: James E. Eldridge, senior applications engineer, Kimre Inc., Miami, Florida, USA.

References:


2. European Fertilizer Manufacturers’ Association, Production of Phosphoric Acid, Booklet No. 4 of 8, Brussels, Belgium, 2000.

3. Centers for Disease Control and Prevention, Division of Oral Health, Engineering Fact Sheet, Community Water Fluoridation, CDC Atlanta, GA.


5. Thomas G. Reeves, PE., Fluorosilicic Acid Dilution Factor, FL-147, CDC Division of Oral Health, Atlanta, GA, 2002


7. Technical discussion between the author and Mr. Alain Dreveton, President, AD Process Strategies SARL, Geneva, Switzerland, alain.dreveton@adpro-stg.com, 2008.