HYDROFLUOROSILICIC ACID AND WATER FLUORIDATION

Water fluoridation is an important preventative measure carried out in much of the western world. It results in some of the hydroxyapatite, $Ca_5(PO_4)_3OH$, of which human tooth enamel is made being replaced by fluoroapatite, $Ca_5(PO_4)_3F$ - a substance significantly more resistant to decay. Thus to protect the teeth of the population, water is often fluoridated. This is usually done with one of three fluorine-containing chemicals (sodium fluoride, sodium fluorosilicate and hydrofluorosilicic acid), but this article focuses on hydrofluorosilicic acid as that is the chemical most commonly used in New Zealand for this purpose.

Hydrofluorosilicic acid manufacture can be viewed as a two-step process, although in reality it is carried out in four steps to ensure that the right concentration of acid is obtained.

Step 1 - Production of SiF_4
The superphosphate production process results in the evolution of carbon dioxide, steam and SiF_4. This SiF_4 is an environmental pollutant and so is removed from the gas stream and used to produce fluorosilicic acid.

Step 2 - Hydrolysis of SiF_4
The SiF_4 is removed from the gas stream by contacting the gas with water droplets. This water hydrolyses the SiF_4 as follows:

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$

The resultant hydrofluorosilicic acid (H_2SiF_6) is used for fluoridating drinking water.

INTRODUCTION

In many cities in the western world, drinking water is fluoridated to help prevent people's teeth from decaying. Fluorine achieves this by replacing hydroxyapatite ($Ca_5(PO_4)_3OH$) with fluoroapatite ($Ca_5(PO_4)_3F$). Fluoroapatite is more resistant to acid attack and thus teeth which contain even a small proportion of fluoroapatite are less likely to decay. The relevant reactions are as follows:

Tooth decay: $Ca_5(PO_4)_3OH(s) + 4H_3O^+(aq) \rightarrow 5Ca^{2+}(aq) + 3HPO_4^{2-}(aq) + 5H_2O(l)$

Fluoridation: $Ca_5(PO_4)_3OH(s) + F^-(aq) \rightarrow Ca_5(PO_4)_3F(s) + OH^-(aq)$

Fluoridation of water in New Zealand is largely accepted, and there are only two major cities that do not adjust the fluoride level of their water supply. Referendum is becoming the norm for determining public opinion on whether to fluoridate or not.

Three chemicals are in common use for this purpose, namely sodium fluoride, sodium fluosilicate and hydrofluorosilicic acid (HFA).

Sodium fluoride

Sodium fluoride is a white powder, moderately soluble in water (about 3% w/w). For water

fluoridation purposes it is usual to prepare a saturated solution in water and inject this solution into the bulk water. However, sodium fluoride is the most expensive of the three and for this reason is not widely used.

Sodium fluorosilicate

Sodium fluorosilicate is a white powder sparingly soluble in water (about 0.6% w/w). This low solubility means that it is not feasible to use a saturated solution so dry solid is fed into bulk water at the appropriate rate. However, it can be difficult to control small flows of solid and this aspect of fluoridation equipment must be well designed and carefully monitored. Nevertheless, the fluorosilicate is widely used as it is significantly cheaper than the fluoride salt.

Hydrofluorosilicic acid

Hydrofluorosilicic acid has several advantages. Being a liquid, it is easy to handle and to meter accurately into the bulk water. Plant operators do not have to manually handle fine powders. The acid is also the cheapest source of fluorine. However, it is corrosive and tends to fume, particularly at concentrations of above 20%. Its main drawback is that it is a comparatively dilute source of fluoride. 15% acid contains just under 12% fluorine by mass, whereas sodium fluoride contains 47% and sodium fluorosilicate 60%. Over long distance transport costs can make solid chemicals more attractive.

All manufacturers of superphosphate produce hydrofluorosilicic acid as a by-product.

THE HYDROFLUOROSILICIC ACID MANUFACTURING PROCESS

Step 1 - Production of SiF_4

Superphosphate is manufactured by mixing together finely ground phosphate rock and sulfuric acid. A vigorous reaction occurs with considerable gas evolution. The gases given off are mainly steam and carbon dioxide, but there is also a small quantity of silicon tetrafluoride released (seeprevious article). Uncontrolled release of this gas to atmosphere could cause significant pollution so every fertiliser works has a gas scrubber as an integral part of its manufacture plant.

Step 2 - Hydrolysis of SiF_4

Silicon tetrafluoride reacts readily with water, so it is removed from the other gases by a gas scrubber that is essentially a means of contacting the gas stream with finely divided droplets of water. The reaction with water hydrolyses the silicon tetrafluoride according to the equation:

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$

In this way 99% of the fluoride is removed from the gas stream, leaving only a very small quantity to be emitted. These emissions are covered by a discharge permit and less than 0.1 g s^{-1} fluoride is discharged to the atmosphere. The liquid from the scrubber is usually a dilute solution of hydrofluorosilicic acid, with a small amount of solid silica suspended in it. This dilute hydrofluorosilicic acid can be partially substituted for sulfuric acid in the production of superphosphate.

In the New Plymouth works of Farmers Fertiliser Ltd the scrubbing process has been modified so as to produce an acid suitable for water fluoridation. In this works the scrubbing

process is divided into three stages with acid of different concentration in each. This yields an acid containing about 20% H_2SiF_6 which is acceptable to local authorities. The superphosphate article has a flowsheet showing a typical scrubber installation for hydrofluorosilicic acid production. Water and gas are made to flow 'countercurrent' to each other so that gas rich in fluoride is contacted by strong acid and gas weak in fluoride meets very dilute acid. Strong acid is pumped away from the first scrubber and settled to remove silica before being sold.

ENVIRONMENTAL AND FINANCIAL CONSIDERATIONS

This process removes fluoride from the gas stream, thus preventing an environmental hazard, but it does have its problems. The 20% acid is very corrosive to most metals, so scrubbing equipment is more costly than that used with plain water sprays. However, the demand in the North Island is sufficient to justify economic recovery.

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