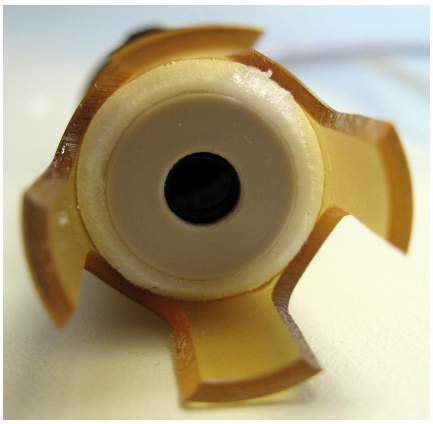
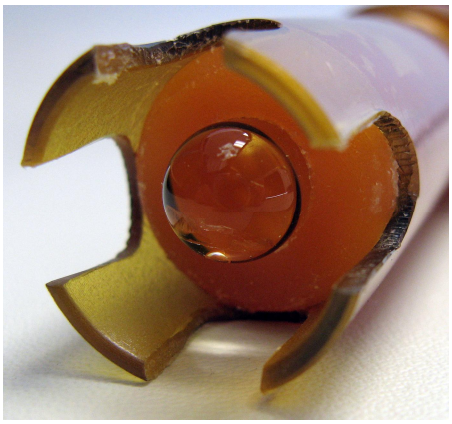
Case Study No. 21 – TOTAL FLUORIDE MEASUREMENTS



AB 6100 Fluoride ISE Sensor



PNHF 6431 pH Sensor

Dual 56 Total Fluoride Analyzer

Inline Continuous Total Fluoride Measurement System using:

- **AB 6100 Fluoride Ion Selective Sensor** for High HF & Low pH Service
- **PNHF 6431 pH Sensor** for High HF & Low pH Service
- **Dual Channel 56 Analyzer**, Transmitter & Controller that computes the **Total Fluoride** from Fluoride ISE & pH sensor inputs

Real-Time Measurement & Control of Wastewater Treatment of Acid Fluoride Etching Media from Metal, Glass and Silicon Wafer Process Applications

SPECIAL FLUORIDE ION SELECTIVE FEATURES

- Specially designed and fabricated fluoride ion selective sensors that are suitable for continuous measurement in samples with a pH as low 0.0 and up as high 11.0
- These low pH service fluoride ISE sensors can withstand strong acid cleaning, typically done with hydrochloric acid (HCl), that is often required to remove calcium fluoride (CaF_2) and various fluorosilicate build-up on the sensing membrane due to the typical wastewater treatment process for acid fluoride etching of metal, glass or silicon wafers

SPECIAL HF RESISTANT pH FEATURES

- The model PNHF 6431 high HF resistant pH sensors are designed and fabricated to allow for determination of pH in these same low pH high fluoride samples of interest for fluoride measurement and supporting the same 0 to 11 pH range as the fluoride ISE sensor
- Industry leading novel HF resistant pH glass formulation allows for accurate process measurements and long pH sensor lifetime in aggressive HF service conditions

SPECIAL FEATURES COMMON TO BOTH FLUORIDE ISE & pH SENSORS

- Fully submersible to any depth with included waterproofing "H" sealing option
- Support for integal preamplifiers and external preamplifier in waterproof J-Box assembly as may be required for that specific installation site (max 100 meters a.k.a. 330 feet)
- All pH, ORP & Ion Selective sensor employ a solid-state conductive cross-linked polymer reference system in a double or triple junction configuration for low-maintenance and long service lifetime with very infrequent calibrations (low drift)
- Rugged ULTEM (Poly-Ether-Imide, a.k.a. PEI) sensor body material of construction
- Available in optional solvent resistant configuration for both Fluoride ISE & pH sensors

SPECIAL TRANSMITTER FEATURES

- Special high HF and low pH service fluoride ion selective (ISE) sensors and pH sensors together with mating dual fluoride/pH systems with second generation 56 analyzer, transmitter & controller allow for real-time continuous determination of total fluoride
- Total fluoride is a computed value from free fluoride ion activity measured by the fluoride ISE sensor with pH value from inline pH sensor. The computed total fluoride is the summation of all fluoride species not chemically bound but independent of pH value.
- All sensors inputs are automatically temperature compensated in the 56 analyzer software
- Use of system is as simple as taking a process grab sample and analyzing it for fluoride and entering this value into the 56 analyzer. This critical grab sample offset calibration procedure ensures good agreement between periodic field or lab analysis and inline readings
- Time delayed offset grab sample calibration feature allows for a time difference between when grab sample is taken from process and when the determined value is entered into analyzer for ease of calibration and accurate offsets (only available in SW 1.18 or higher)
- Total Fluoride 56 Dual Fluoride/pH instrument includes 4 each scalable 4-20mA outputs that can be configured for any measurement monitoring or control purpose
    - A typical setup example would be Output1: Total Fluoride, Output2: Free Floride, Output3: pH; Output4: Temperature although many other configurations are possible
- Local controller functionality with 4 each 5A dry contact relays for simple on/off control (with configurable deadband) all the way to complex time proprotional control algorithms
- HART digital protocol standard allowing for easy remote configuration as well as remote offset grab sample calibration to make ISE maintenance substantially more convenient
- Onboard 30 day datalogging of all measurement, computed parameters (total fluoride) and events to allow for simple operator review of each installation site and to facilitate expeditious troubleshooting. The recorded data can be trended on the large color LCD display or else downloaded to a USB flash drive for compliance monitoring at sites where the analog 4-20mA or HART outputs are not yet integrated with the main PLC or SCADA

The Problem

A major semiconductor company operated an acid fluoride wastewater treatment system and so needed to monitor their fluoride levels at various stages of their process to ensure proper system operation as well as compliance with local discharge regulations. Very many electrochemical and sampling analyzer vendors that sold fluoride measurement system could not supply fluoride ion selective and pH sensors that could survive in low pH conditions in the presence of high levels of fluoride. This lead to frequent fluoride and pH sensor replacement and a high cost of ownership of these existing systems. In some cases the normal condition of the measurement points in the wastewater treatment system was of a neutral type pH condition (typically above 5.5) but during periodic process upsets the pH could become quite depressed (often down as low as 1 or 2) for extended periods of time leading to a wholesale loss of entire sets of sensors for such larger treatment facilities. In either case the inability to support the low pH condition in the presence of high levels of fluoride led to serious long-term costs for the customer.

Alternatively, even for applications that do not have low pH conditions it is quite common that due to the nature of treating acid fluoride waste (often with calcium chloride – $CaCl_2$ – or calcium hydroxide – $Ca(OH)_2$ –) there can be a rather substantial build-up of insoluble solids that must be removed from the sensor and this is only possible with performing strong acid cleaning. A rather typical example is the removal of calcium fluoride (CaF_2) or fluorosilicates by means of strong hydrochloric acid (HCl) cleaning media. Many other cleaning approaches are possible but most all involve the use of strong acids that can shorten the competitor's sensor lifetime. In this way when the wastewater treatment systems were under heavy load, the frequency of cleaning required to remove the build-up was high the sensor lifetime short during these intense load periods. This also led to high residual cost of owernship for these competitor's inline fluoride ISE measurement systems.

Many batch treatment reactors and first-stage neutralization points experience oscillations in pH that are characteristic of that stage of the treatment process and variations in the levels of load from the acid flouride etching systems themselves. In such cases to get a good sense of the overall load to be used by the fluoride wastewater treatment system you must know the sum that is defined by all of the total possible reactive fluoride species present. This sum is the free fluorie ions together with the fluoride ions bound by hydrogen as HF. Since this total reactive specis sum cannot be measured directly inline, you must perform pH compensation to compute it from the measured free fluoride ions themselves (as measured in real-timefrom the fluoride ion selective sensor) together with the inline pH sensor to determine the pH level. The pH compensation algorithm can then compute the total reactive fluoride species (free fluoride ions – F^- – and bound HF form) that must be accounted for by the fluoride wastewater treatment system.

Lastly, some parts of the manufacturng process itself used relatively weaker acids (but pH levels still in the rather low 1 to 2 range) and lower levels of fluoride (meaning below 1000ppm) so that they can be run as continuous acid etching baths rather than batch aciding systems. For these continuous acid fluoride etching baths the computed total fluoride defines the amount of HF or ammonium bifluoride (ABF) to be added and the pH defines the amount of acid to be added. While these continuously controlled acid fluoride etching applications are less common than the batch variety (where there exists a starting strong acid and strong fluoride bath where the reagents are consumed until they are no longer effective enough to accomplish their etching purpose, be it for metal, glass or silicon wafers for semiconductor chips or solar cells) it is also desirable to use the same set of fluoride and pH sensor and total fluoride controller to measure these processes as well. In short a uniform solution to handle all of the inline process total fluoride and pH measurement needs was required.

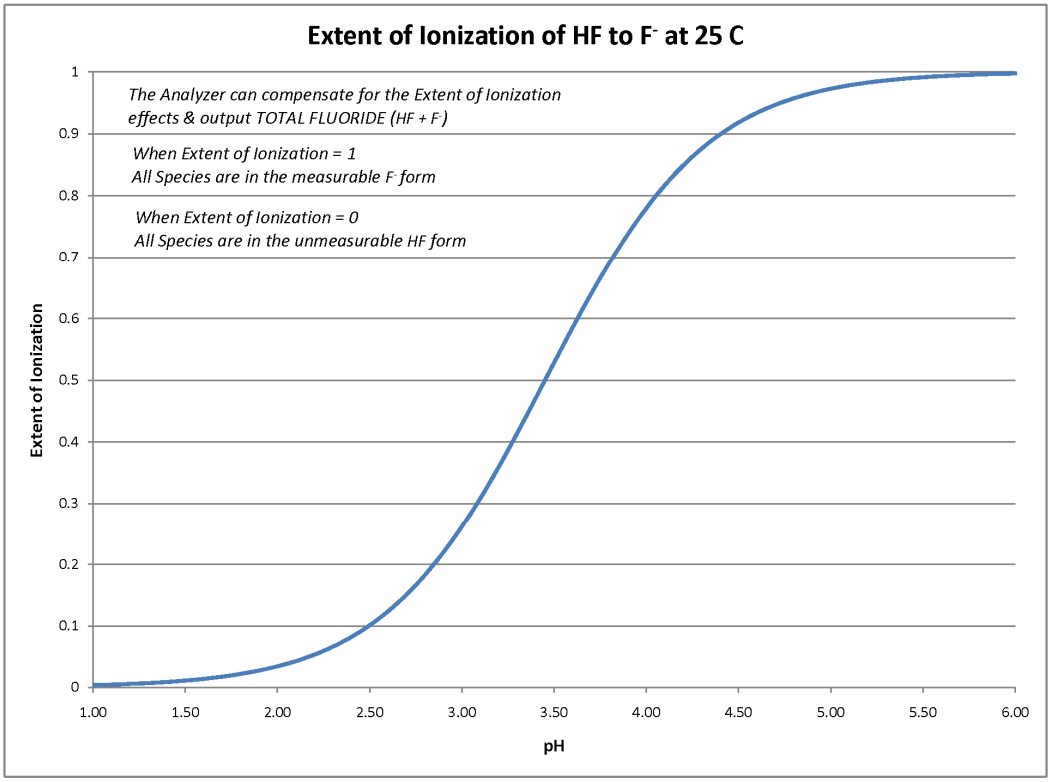
The Solution

The solution for these measurement needs was a combination of customizations involving both specially designed and fabricated fluoride ion selective (ISE) & pH sensors as well as some rather specialized instrumentation and controllers. First and foremost some rather customized fluoride ion sensing elements are made such that they can readily withstand strong acid exposure (be it from the process media or cleaning solution) for extended periods of time. To our knowledge there is no other supplier that fabricates such a highly customized and extensively industry field test fluoride ion selective sensing element for acid service. Combined with this specialty fluoride ISE sensing element is a conductive polymer solid-state reference technology that enabled use up to 70 degrees Celsius (170 degrees Fahrenheit) even at very low pH (down to 0) and high fluoride levels (supported up to 19,000ppm). There are no other suppliers that can support these conditions.

Nearly just as important is accurate pH measurement in such acid fluoride conditions. While there are a variety of non-glass based pH sensors that are sometimes used for the measurement of pH in such low pH fluoride media, in truth none of them are effective and reliable enough to serve the sensitive analytical needs for such wastewater control and acid etching systems. With this in mind, a very special high HF low pH service sensing glass was designed and once again extensively field tested to be as resistant to these conditions as possible within the confines of using a nominally "glass" based pH sensor. The word glass is in quotes because this nomenclature is rather misleading. In truth pH "glass" is not truly "glass" but rather a glass-like material that has a linear response to pH and so can be used for such analytical measurement applications. This special high HF resistant pH glass is once again combined with the solid-state reference system to assure long-life low maintenance operation and ruggedness to the necessary periodic cleaning procedures. The waterproofing seal style "H" is added to both the fluoride & pH sensors to ensure a full submersible assembly (see photos below).

The two pictures above show the model AB 6100 low pH service fluoride ion selective sensor (on left in both photos) and PNHF 6431 high HF (low pH) service pH sensor (on right in both photos) with the waterproofing "H" submersible option. Both sensors have mlutiple special features that make them suitable for use in low pH service conditions in the presence of high levels of fluoride. Among these special features includes a unique sealing washer for the fluoride ISE sensor (close-up on first page photo on the far left) as well as the CPVC cemented vinyl tubing that ensures an integral seal on the cable for very long service life.

Having the specially designed HF resistant low pH service sensors described above is not sufficient to fulfill these measurement requirements, however. A suitable instrument is also require to complete the analytical measurement that can determine the total fluoride and can serve as a simple transmitter, local controller or complete digital datalogger and measurement node. First and foremost a dual channel fluoride and pH instrument is required that can take the free fluoride ions measurement by the fluoride ion selective sensor together with the pH levels from the HF resistant pH sensor and combine them to compute the total fluoride.



The graph above show the impact of pH on the extent of ionization of dissolved HF gas to fluoride ions. The extent of ionization defines the percent of the weak acid HF that the ion selective sensor can detect. On the vertical axes if the extent of ionization is 0.00 then none of the fluoride species is in the measurable form while if the extent of ionization is 1.00 then all of the fluoride species is in the form that is measurable by the fluoride ISE sensor. The blue colored line demonstrates the portion which is in the measurable free floride ion form at that given pH (the extent of ionization) which is also called the “free fluoride”. The “total fluoride” computed by the Dual 56 Fluoride/pH analyzer, transmitter & controller is the value as though all 100% of fluoride were in the form such that it was measurable by ISE sensor. This “total fluoride” is the species that is of genuine interest for such measurement and control applications.

In addition to the ability to compute the total fluoride as detailed in the page above, there are some additional requirements for such applications to fulfill these inline analytical measurement needs. These include the ability to support long cable runs for fully submersible type sensors. In many cases this means the need for integrated preamplifiers inside the sensor as well as special shielded cables (even when preamplifiers are used) to support use in high noise areas. The 1056, 1057 and 56 ISE analyzers all support pH, ORP and ISE sensors both without integrated preamplifiers at cable lengths up to 6 meters (20 feet) and when used with an integrated preamplifier up to 100 meters (330 feet). The ability to support extended cable runs either through the use of an integral preamplifier inside the sensor or via a bridged external waterproof J-Box assembly is often critical to

make many field applications feasible and easy to maintain. Another common approach in addition to having an integral preamplifier inside the sensor connected directly to the transmtiter or else a sensor without a preamplifier bridged across an external preamplifier in a waterproof J-Box is to use a sensor with an integral preamplifier and to bridge it across a waterproof J-Box using just ordinary terminal strip connections (this can be quite convenient for high noise areas that need convenient sensor replacement procedure). In addition to such extended cable length support, naturally at minimum a 4-20mA analog output is required for all measurement species of interest namely the total fluoride, free fluoride, pH and temperature. In addition, in many cases even when the PLC or other robust integrated control system is used, local alarm relays are still desirable in either total fluoride or free fluoride units. Furthermore, for some (typically remote) installation points local control via PID or time proportional (TPC) relays is also needed. Lastly, for many modern semiconductor plants there is the need for HART or ProfiBUS digital data communications in addition to the scalable analog 4-20mA outputs. All of the analyzer functionality detailed above in addition to major agency approvals such as FM, CSA, and UL are available for Class I, Divison II areas for panel, wall or pipe installation styles are possible using either the 1056, 1057 or 56 ISE analyzers, transmitters and controllers.

Typical Sensors Used for These Measurements

Sensors WITHOUT preamplifiers for Shallow Tank Installations with Standpipe for Submersion Use

Model: AB 6100-1000-15-TL-WPH Fluoride (F^-) Ion Selective (ISE) Sensor for Low pH Service & Acid Cleaning Use
Description: Industrial 1”-1¼” MNPT ULTEM Bodied Submersible Fluoride Ion Selective Sensor with integrated 1000 Ohm Platinum TC Element; 15 feet cable (~5 meters); Waterproofing "H" to support fully submersible installs in acid media

Model: PNHF 6431-1000-15-TL-WPH High HF Resistant **pH** Sensor for Low pH Service & Acid Cleaning Use
Description: Industrial ¾”-1” MNPT ULTEM Bodied Submersible High HF Resistant pH Sensor with integrated 1000 Ohm Platinum TC Element; 15 feet cable (~5 meters); Waterproofing "H" to support fully submersible installs in acid media

Sensors WITH preamplifiers for Deep Tank Installations with Standpipe for Submersion Use

Model: AB 6100-1056-35-BL-WPH Fluoride (F^-) Ion Selective (ISE) Sensor for Low pH Service & Acid Cleaning Use
Description: Industrial 1”-1¼” MNPT ULTEM Bodied Submersible Fluoride Ion Selective Sensor with integrated Pt1000 TC & Model 1056/1057/56 compatible preamplifier with special shielded jacket for high noise areas and rugged field use; 35 feet cable (~10 meters); Waterproofing "H" to support fully submersible installs in acid media

Model: PNHF 6431-1056-35-BL-WPH High HF Resistant **pH** Sensor for Low pH Service & Acid Cleaning Use
Description: Industrial ¾”-1” MNPT ULTEM Bodied Submersible High HF Resistant pH Sensor with integrated Pt1000 TC & Model 1056/1057/56 compatible preamplifier with special shielded jacket for high noise areas and rugged field use; 35 feet cable (~10 meters); Waterproofing "H" to support fully submersible installs in acid media

Typical Analyzer Configurations Used for these Measurements

Model: **56-XX-22ISE-32-YY** (**Fluoride / pH – Total Fluoride**)
Description: Dual Channel Fluoride & pH Total Fluoride Analyzer, Transmitter and Controller
Outputs: 4 each 4-20mA Outputs, With relays standard, HART standard, PID/TPC standard, ProfiBUS Optional

Model: **1056-XX-22ISE-38-YY** (**Single Channel Fluoride** - Where the pH is ALWAYS above 5.5)
Description: Single Channel Fluoride Analyzer, Transmitter and Controller
Outputs: 2 each 4-20mA Outputs, Available with or without relays, HART & ProfiBUS Optional

Model: **1057-XX-22ISED-32-42** (**Fluoride / pH / pH** - Where the pH is ALWAYS above 5.5)
Description: Triple Channel Fluoride, pH & pH Analyzer, Transmitter and Controller For Redundant pH Measurement
Outputs: 4 each 4-20mA Outputs, With relays standard

XX is the power supply and YY is the output option. ISE configurations must be specified at time of order. Complete ISE systems only available directly from ASTI as complete systems. ISE sensors are NOT available for sale without mating ISE analyzer complete by ASTI. Applications must be validated by ASTI factory prior to sale. Industry references available upon request.

Last Revised December 28, 2012