

Breakthrough Nitrogen Oxides Chemistry Saves Costly Scrubber Addition at ShinEtsu America

By using an innovative chemistry to treat nitrogen oxides (NOx) emissions, silicon wafer manufacturer ShinEtsu America, Inc., (SEH) avoided adding a costly new scrubber. The scrubbing solution, a drop in replacement for sulfide chemistries, enables SEH to meet air and water emissions requirements and eliminate nuisance odors at its Vancouver, WA, facility.

The unique scrubbing solution was developed by Bionomic Industries Inc. (Mahwah, NJ) to meet the need for a safe, easy to handle high efficiency nitrogen dioxide scrubbing solution that eliminates production of toxic and odoriferous hydrogen sulfide gas. It is extremely cost effective since it eliminates the need for a polishing scrubber stage to remove hydrogen sulfide gas, lowering capital equipment, utility and chemical operating costs.

Community Commitment

SEH had been using sodium hydrosulfide (NaSH) in its NOx scrubber to treat emissions from its cut wafer etching process. NaSH use had maintained permitted levels of hydrogen sulfide and opacity requirements, but, even very low concentrations resulted in nuisance odors. The plant's employees as well as the surrounding neighborhood, including an elementary school, often commented on the unpleasant smell.

SEH Facilities Engineer Bryan Trotter explains, "Since we are concerned about our employees' work environment, and have a close relationship with the school and our other neighbors, we began to explore what we could do pre-emptively to improve the situation.

"We investigated the feasibility of adding an additional scrubber at the end of our existing unit to remove small concentrations of hydrogen sulfide gas. We learned we would have to make a large capital investment and gain a very small return. Additionally, the fact that this would have to be done within a small physical area, which would further complicate and add cost to the project."

SEH considered converting the scrubber to use hydrogen peroxide. After extensive testing, hydrogen peroxide was eliminated from considerations because it showed very poor results and had a high operating cost. That led the company to assess the suitability of a solution would be an excellent drop in replacement for NaSH and provide SEH with a host of benefits.

SEH bought a test amount of the chemical and, after contacting the air and wastewater permitting authorities, arranged for on-site testing. When the scrubber was run through all the different production loops, the scrubbing solution controlled the NOx emissions well within the permit limit. Hydrogen sulfide and other sulfur compound testing was done on the exhaust to determine if there was a reduction in the sulfur compounds. Since the company had done similar testing while using sodium hydrosulfide, it was able to see that unlike sodium hydrosulfide, the product virtually eliminated sulfur compounds in the exhaust.

"Since the scrubbing solution has virtually no smell, it eliminated the unpleasant odor that operators were subjected to when even a drop of NaSH contacted their protective clothing. It also eliminated the odor that the NaSH product would infuse throughout the facility when it was pulled into the building's air handlers."

Solution Means Savings

Trotter explains, "Our initial test results showed that the product would work well, it would involve minimal modification to our existing scrubber and infrastructure and it would basically be a drop in replacement once we gained permit approval from the air and wastewater agencies. Both organizations were very willing to help us with that transition since we demonstrated that the product eliminated the nuisance odor and the wastewater by-product had less potential for creating sulfur acid gases in the sewer system.

"A key advantage of this solution is that we were able to retain an older manufacturing plant that is close to depreciated, without making a major capital investment. If we had

to make that investment, it would have been greater than what we are spending for this system.

"The horizontal scrubber, located on the second floor of our facility, has a small footprint that cannot accommodate a vertical scrubber. In addition to the physical and construction constraints, there would have been considerable engineering and design time involved to add a new scrubber. This would have resulted in the challenge of remaining in production during the changeover. In our business, downtime is not an option and construction would have required a significant downtime.

"Since we began using this chemistry in September 2003, we've learned that there are opportunities for future cost reductions of approximately 5 to 10 percent. We are exploring transitioning to obtain the product in bulk supply rather than in small containers. We will investigate running the system at a lower pH to capture some caustic operating cost savings. Currently, we're running at 12.5, but our permit limit is set at no lower than 11."

The Process

During SEH's cut wafer etching process silicon wafers are etched in a bath including nitric acid, acetic acid and hydrofluoric acid, which creates nitrogen oxide gases.

In the scrubber, the exhaust gas travels horizontally and the scrubber liquor travels vertically. Although the design of the scrubber was not changed, at the same time the solution was introduced. SEH made improvements to the scrubber including reducing air-flow to lower the velocity and increase the residence time. It also converted the fan to variable speed and made instrumentation upgrades.

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Trotter reports, "We are using the product in the first and second, which are actually the second and third stages of the process. In the first stage, which is a prescrubbing phase, hydrofluoric, acetic and nitric acids are removed before the first stage begins.

"NaSH was very sensitive to any low pH stream contacting it and would release hydrogen sulfide. Because of the old design of the scrubber, if any acid gas that was able to bypass into the first stage and hit the NaSH, it would trigger the response. Also, if any of the scrubber recirculation liquid from the first stage was able to back up into the prescrubber, there was a potential for hydrogen sulfide generation. This chemistry's wider band of pH tolerance has proven to be much more robust in terms of being able to handle some amounts of acid gas. If there are small pockets of acid gas that contact the product, it does not release the hydrogen sulfide until it reaches an extremely low pH."

To measure compliance, SEH has a continuous NOx analyzer on the exhaust side at the back end of the scrubber. Recommended use of the product is to pre-dose the stages to a predetermined amount and then continue to add the product based on ORP measurement. SEH had some concerns about product deterioration since it only runs the process six to eight hours and it also blows down each stage so there is a loss of chemical. To address the situation, the company installed metering pumps controlled through a PLC, which receives a signal from the NOx analyzer, to add the chemical to each stage. When the process reaches five parts per million (ppmv) of nitrogen oxides, the PLC turns on the two chemical pumps and begins to add chemicals into the scrubber recirculation lines. The pumps are sized to add sufficient chemical quickly enough to match the NOx coming into the scrubber. This process minimizes the amount of chemical put in and also prevents waste between production cycles.

Trotter adds, "We've added a few features to the PLC program to enhance our control. For example, if for some reason we get up to a higher value approaching our permit limit, the PLC will automatically turn on the diaphragm pump and dose it with a higher volume to bring the emissions down."

Sharing the Advantage

While the semi-conductor industry traditionally retains a low profile, SEH believes that sharing its experience can benefit others in and out of its industry in addressing environmental concerns and issues, as well as community responsibilities.

Trotter concludes, "This solution has enabled us to provide employees and the community with a more pleasant environment. At the same time, its innovative technology has made it possible for us to save the cost of a large capital investment by retrofitting our existing scrubber while maintaining our compliance with air and wastewater permit limits."

SEH America, Inc. is part of the largest producer of semiconductor silicon in the world, Shin-Etsu Handotai (SEH), Ltd., headquartered in Tokyo, and is an integral part of the ShinEtsu group. In the Vancouver, Washington facility, we manufacture single-crystal silicon ingots, polished and epitaxial wafers, and provide service and engineering support for customers. Our worldwide reputation for quality is based on global technical innovation in facilities located in Japan, Malaysia, Europe, Taiwan, and the U.S.A.

SEH is the world-leader in the manufacturing of silicon wafers for the semiconductor industry. Sliced from an ultra-pure crystalline ingot and then polished, silicon wafers are processed by our customers through the addition of circuit patterns arranged in tiny squares commonly referred to as "computer chips." These chips are then separated and packaged into electronic components that are at the heart of many products, including computers, lasers, automotive electronics, telecommunications, and many consumer products.

Bionomic Industries Inc., founded more than two decades ago, has been supplying pre-engineered air pollution control products, "prepackaged" skid-mounted ScrubPac™ scrubber systems, HEI™, wet electrostatic precipitator and dry collection systems for a wide range of air pollution abatement and product recovery applications. The company is at the forefront in developing new products through innovative technologies that meet the ever-changing needs for more efficient devices and chemistries to solve challenging air pollution problems. Bionomic's customers include the chemical, pharmaceutical, food processing, pulp and paper, wood products, metallurgical, iron and steel, mining, electronic, hazardous waste, general manufacturing, municipal, power and mining industries.

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