ONSTREAM AMMONIA ANALYZER AT AGRICO DAP PLANT

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TEXT OF PRESENTATION TO THE CENTRAL
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AGRICO FIRST BEGAN TO INVESTIGATE ONSTREAM AMMONIA ANALYSIS OF DAP STACK GAS IN THE FALL OF 1973. AT THAT TIME THE FAUSTINA PLANT AT DONALDSONVILLE, LOUISIANA HAD TWO DAP TRAINS, EACH CAPABLE OF PRODUCING ABOUT 1000 TONS PER DAY OF GRANULAR DAP PRODUCT.

A THIRD DAP UNIT HAS SINCE BEEN COMPLETED TO RAISE THE TOTAL PLANT CAPACITY TO 4000 TPD.

OUR ORIGINAL EFFORTS IN AMMONIA MONITORING HAD BEEN MANUAL, AND FAIRLY CRUDE. HOWEVER, THE RESULTS WERE ACCURATE ENOUGH TO VERIFY THE FACT THAT AMMONIA LOSSES COULD VARY CONSIDERABLY OVER A PERIOD OF TIME WITH CHANGING PROCESS CONDITIONS. THE SAMPLING SYSTEM CONSISTED OF A VACUUM SOURCE (FAN SUCTION), A RUBBER SAMPLE LINE, A SAMPLE PROBE OF METAL TUBING, A MANUAL FLOWMETER TO MEASURE SAMPLE SIZE, A WATER KNOCKOUT, AND A BORIC ACID ABSORBER. STACK GAS WAS DRAWN MANUALLY FROM THE FAN DISCHARGE DUCT FOR A KNOWN LENGTH OF TIME AT A MEASURED RATE THROUGH THE BORIC ACID ABSORBER. THE AMOUNT OF AMMONIA WAS DETERMINED BY BACK TITRATION WITH STANDARD HYDROCHLORIC ACID AS IN THE KJELDAHL ANALYTICAL METHOD FOR AMMONIACAL NITROGEN. THIS INFORMATION WAS COMBINED WITH PITOT MEASUREMENTS OF STACK GAS FLOW TO ARRIVE AT A MEASURED AMMONIA LOSS IN TONS PER DAY.

USING THE DESCRIBED APPARATUS, WE MEASURED THE AMMONIA LOSS FROM THE FUME SCRUBBERS ON A SPOT BASIS ONCE PER DAY. AFTER SOME TIME OF RECORDING SPOT LOSSES RANGING ALL THE WAY FROM 3 TO 30 TONS PER DAY, THE SAMPLE FREQUENCY WAS INCREASED. THE NEED FOR MORE CONTINUOUS MONITORING & A LOSS REDUCTION PROGRAM BECAME VERY OBVIOUS.

EXPLORATORY CONTACT WAS MADE WITH THE DUPONT COMPANY. THEIR 460 ANALYZER SYSTEM WAS ALREADY ON THE MARKET TO MONITOR SO_2 IN STACK EMISSIONS FROM POWER GENERATING STATIONS, SULFURIC ACID PLANTS, NON-FERROUS SMELTERS, SULFUR RECOVERY OPERATIONS AND SULFITE PULP MILLS. THIS SYSTEM USES A SPLIT-BEAM PHOTOMETRIC ANALYZER THAT MEASURES DIFFERENTIAL UNTRAVIOLET LIGHT ABSORPTION AT TWO DIFFERENT WAVELENGTHS. DIFFERENT WAVELENGTHS ARE USED FOR DIFFERENT GASES,

DEPENDING ON THE DESIRED COMPONENT. THE DUPONT PEOPLE FELT THAT THE 460 SYSTEM COULD BE ADAPTED TO AMMONIA ANALYSIS EVEN THOUGH AGRICO'S STACK GAS CONTAINED ABOUT 40% WATER VAPOR, ENTRAINED SCRUBBER LIQUOR, AND OTHER PARTICULATE MATTER IN ADDITION TO THE AMMONIA.

A TWO POINT 460 SYSTEM WAS PURCHASED IN EARLY 1974 TO ALTERNATELY MONITOR THE EXIT FUME STACKS OF THE TWO EXISTING DAP UNITS. THE SAMPLE PROBE IS STACKMOUNTED AND EXTENDS ABOUT HALF WAY INTO THE STACK. THE INLET TO THE PROBE IS SHIELDED FROM EXCESSIVE PARTICULATE ENTRAINMENT BY A WIRE MESH SHIELD. SAMPLE IS DRAWN AT 3" HG VACUUM THROUGH A 1/4" I.D. TEFLON HEAT-TRACED (105°C) SAMPLE LINE TO THE ANALYZER. A TEMPERATURE CONTROLLER MAINTAINS THE SAMPLE LINE AT THE DESIRED TEMPERATURE TO PREVENT SAMPLE CONDENSATION BEFORE REACHING THE ANALYZER. INCIDENTALLY, THE SAMPLE RUN FROM STACK TO ANALYZER IS AROUND 90-125 FT. I BELIEVE DUPONT RECOMMENDS A MAXIMUM OF ABOUT 200 FT. THE SAMPLE PASSES THROUGH A LIQUID KNOCKOUT POT, THE PHOTOMETRIC READING CELL, AND THEN TO EXHAUST. THE ANALYZER IS CALIBRATED TO MEASURE THE AMMONIA CONTENT OF THE SAMPLED GAS IN PERCENT BY VOLUME. OUR FIRST UNIT IS CALIBRATED TO MEASURE 0-2% AMMONIA, ALTHOUGH THERE IS PROBABLY ENOUGH FLEXIBILITY TO CHANGE THIS BY A FACTOR OF 5 WITHOUT ALTERING THE LINEARITY OF THE PHOTOMETRIC ABSORBANCE. MR. HURLEY CAN CORRECT ME ON THAT POINT IF I AM IN ERROR. WE HAVE ALSO USED STANDARD STACK GAS FLOWS PLUS MEASUREMENTS TO RELATE THE PERCENT BY VOLUME ANALYSIS TO TONS PER DAY AMMONIA LOSS. DAVE HURLEY HAS COVERED THE BASIC MECHANISM OF THE ANALYZER ITSELF.

SEVERAL PROBLEMS WERE INITIALLY ENCOUNTERED WITH THE UNIT, AS MIGHT BE EXPECTED. SOME OF THESE PROBLEMS AND OUR SOLUTION TO THEM ARE AS FOLLOWS:

(1) THE UNIT WAS INADVERTANTLY DELIVERED WITH THE WRONG SIZE SAMPLE CELL FOR AMMONIA ANALYSIS. ASSISTANCE WAS REQUIRED FROM DUPONT TECHNICAL PERSONNEL TO MAKE THE NECESSARY CELL MODIFICATIONS IN THE FIELD.

(2) THE ORIGINAL WIRE MESH PROBE SHIELD WAS TOO FINE, RESULTING IN FREQUENT PROBE PLUGGAGE. A MORE OPEN MESH WAS SUBSTITUTED.

(3) THE 20# BLOWBACK AIR WAS FOUND TO BE INSUFFICIENT TO COMPLETELY CLEAR THE PROBE DURING THE ZERO CYCLE BETWEEN STACK ANALYSES AND AFTER EXTENDED OPERATION. DUPONT DESIGNED AND FURNISHED HIGH PRESSURE AIR (100#) BLOWBACK ATTACHMENTS FOR THE PROBE TO CLEAR IT PERIODICALLY AS THE SAMPLE FLOW BECAME RESTRICTED. THE INITIAL HIGH PRESSURE BLOWBACK REQUIRED MANUAL SWITCHING AT THE STACK CONNECTION. A REMOTE HIGH PRESSURE SWITCHING MECHANISM IS PRESENTLY AVAILABLE. IT IS ACTIVATED BY A BUTTON ON THE CONTROL PANEL.

(4) MAINTENANCE PERIODS ON THE DAP TRAINS SOMETIMES GENERATED AN EXCESSIVE AMOUNT OF PARTICULATE MATTER WHICH FURTHER CONTRIBUTED TO PROBE PLUGGING. A SAMPLE CUTOFF SWITCH WAS INSTALLED TO REDUCE PLUGGING DURING MAINTENANCE AND STARTUP PERIODS.

(5) THE ANALYZER WAS ORIGINALLY FURNISHED WITH QUARTZ LENSES. THESE WERE ETCHED FAIRLY RAPIDLY BY THE FLUORINE IN THE STACK GAS. A CHANGE WAS MADE TO SAPPHIRE LENSES WHICH WE HAVE FOUND TO BE QUITE SATISFACTORY.

AS ONE MIGHT GATHER, MOST OF OUR EFFORTS ON ANALYZER IMPROVEMENT HAVE BEEN CONCENTRATED ON THE SAMPLING SYSTEM ITSELF. EXCEPT FOR THE EARLY SAMPLE CELL MODIFICATION, THE SOLUTIONS TO ESSENTIALLY ALL OUR ANALYZER MALFUNCTIONS HAVE BEEN FOUND IN THE SAMPLE ACQUISITION AND TRANSPORT SYSTEM. EXCEPT FOR NORMAL AND EXPECTED MAINTENANCE, SUCH AS LAMP REPLACEMENT, THE ANALYZER ITSELF HAS BEEN ESSENTIALLY TROUBLE FREE.

ADDITIONAL OPERATING PROBLEMS THAT HAVE BEEN ENCOUNTERED IN THE SAMPLING SYSTEM ARE:

(1) FAILURE OF SAMPLE HEATERS IN THE TEMPERATURE CONTROLLER AND ANALYZER CABINET

(2) AIR LEAKAGE THROUGH BREAKS IN THE SAMPLE LINE ITSELF, CAUSING LOW ANALYSES

(3) OUTSIDE AIR LEAKAGE INTO THE SAMPLE PROBE BECAUSE OF HOLES IN THE STACK ADJACENT TO THE PROBE

(4) POOR SEALS AT THE CONNECTION OF THE SAMPLE LINE TO THE PROBE, WHICH ALSO CAUSED AIR LEAKAGE

ON THE BASIS OF OUR EXPERIENCE WITH THE FIRST DUPONT 460 ANALYZER, AGRICO PURCHASED A SECOND ANALYZER FOR THE NEW DAP TRAIN WHICH CAME ONSTREAM IN 1975. THE FIRST TWO-POINT ANALYZER HAD BEEN PLACED ON THE TWO EXIT STACKS, PRIMARILY TO MONITOR AMMONIA LOSSES. THE SECOND ANALYZER WAS DESIGNED TO OBTAIN PROCESS INFORMATION AS WELL AS TO MEASURE STACK LOSSES. THE SECOND ANALYZER IS A THREE - POINT UNIT. ONE SAMPLE POINT MONITORS AMMONIA LOSSES FROM THE EXIT STACK AS WITH THE FIRST ANALYZER. THE SECOND AND THIRD SAMPLE POINTS ARE FOR PROCESS MEASUREMENTS SUCH AS SCRUBBER EFFICIENCIES.

IN CONCLUSION, I WOULD LIKE TO SAY THAT WE HAVE FOUND THE DUPONT 460 SYSTEM TO BE A REASONABLY EFFECTIVE MONITOR FOR AMMONIA IN DAP STACK GASES. THE SAMPLING SYSTEM, OF NECESSITY, HAS REQUIRED A FAIR AMOUNT OF MAINTENANCE ATTENTION. THIS IS RATHER OBVIOUS IN VIEW OF THE SEVERE STACK ENVIRONMENT AND THE SAMPLE COMPOSITION. ROUTINE PREVENTIVE MAINTENANCE ON THIS PART OF THE MONITOR, AND ON A FREQUENT TIME CYCLE, IS A MUST FOR THE SYSTEM TO BE RELIABLE. THE ANALYZER ITSELF IS BOTH RELIABLE AND RUGGED. REPAIRS ARE FAIRLY ROUTINE AND RELATIVELY INFREQUENT. CALIBRATION AND ROUTINE CLEANING ARE THE PRIMARY MAINTENANCE ITEMS ON THE MEASUREMENT SECTION OF THE ANALYZER.

THANK YOU VERY MUCH FOR YOUR ATTENTION. THE OPPORTUNITY TO ADDRESS THE GROUP IS CERTAINLY APPRECIATE.

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The Du Pont 46X Analyzer System is one of a series of instruments which is designed for process and emission monitoring. The Model 46X system consists of the Du Pont Model 400 Photometric Analyzer, Associated Sample System and Nema 3R Housing. Variations of the Model 46X system have been widely used in sulfuric acid, nitric acid, and fossil-fired electrical generator plants to measure sulfur dioxide and/or nitrogen oxides for the purpose of conforming to governmental regulations. An adaptation of the Model 46X Analyzer System is installed at the Agrico Chemical Company in Donaldsonville, LA to monitor ammonia at various sample points in the plant's diammonium phosphate production processes. This part of the presentation will describe the Model 400 Photometric Analyzer, and show how it is incorporated into the Model 46X system to measure gaseous ammonia.

The Du Pont Model 400 split-beam analyzer operates on the principle of absorption of ultraviolet radiation by selected chemical components. Radiation from a light source passes through a sample cell and into a photometer, where it is split by a semi-transparent mirror into two beams. One beam is directed to a measurement wavelength phototube through an optical filter which excludes all wavelengths except the measurement wavelengths. The other beam is directed to a reference wavelength phototube through another optical filter which excludes

all wavelengths except a reference wavelength. Both wavelength signals are converted into electrical signals which are individually proportional to the light intensity of each beam. An amplifier system compares the signal from each beam to provide a single photometer output that is linearly proportional to the concentration of the sample. By utilizing the patented split-beam technique, changes in light source intensity, sample cell window cleanliness, and suspended foreign matter have minimal effect on the analysis. Any of these optical variations affect both beams in a similar manner and are compensated for automatically. By use of the split-beam technique, the Model 400 Analyzer responds accurately and linearly to concentration change.

In the typical Model 46X system, the sample enters the analyzer through a 316 stainless steel mesh filter located at the end of the stack probe, passes through heated TFE teflon tubing into a liquid trap for removal of heavy condensate, and then flows through the Du Pont Model 400 Analyzer where the ammonia analysis is made. An air aspirator made of TFE teflon is used to draw the sample continuously from the stack. On an automatic time cycle basis, instrument air reverse flows through the sample line to clean the stack filter and simultaneously passes through the photometric analyzer where compensation for electrical and optical drift is automatically made. A control station, located in a control room or office, is used to periodically perform light source decay and window cleanliness checks. Occasional lamp replacement and sample cell cleaning are the only periodic maintenance requirements on the photometric analyser. The only periodic

maintenance requirements on the sample system consist of occasional cleaning of the sample probe.

The Model 46X system incorporating the Model 400 Photometric Analyzer and associated Sample System has been proved in over 400 installations to measure sulfur dioxide and/or nitrogen oxides in process and stack gases. An adaptation of the Model 46X system configured to optically measure gaseous ammonia has been used in the diammonium phosphate production processes. Operational experience of the two Model 46X systems presently installed at the Agrico Chemical Company in Donaldsonville, LA to sequentially measure ammonia in their diammonium phosphate processes will also be discussed in this presentation.