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The Nucleus of Quality Air Monitoring Programs

Hydrated vs. Dehydrated Silver Zeolite

A Response to an off Gas Hydrogen Explosion at the LaCrosse Boiling Water Reactor in March 1986 During Air Sampling Activity Utilizing Silver Zeolite

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Rev: 14 March 2003

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I. INTRODUCTION

The LaCrosse BWR event is described in NRC bulletin 50-409 identified and introduced concerns over the use of silver zeolite cartridges in post-accident sampling applications where hydrogen may be present.

A summary of the event description is as follows:

General:

— Sampling was being performed to determine the efficiency of an off gas charcoal filter
— Silver zeolite cartridge was being utilized for collecting I-131 in order to avoid interferences of entrained noble gases
— An explosion occurred 2-4 minutes after sampling commenced. Employee heard an explosion and saw a blue flash.

Event Observations:

— Technician noted water droplets in tygon tubing between the silver zeolite cartridge and the pump shortly after commencing the sampling operations
— There was a momentary increase in stack noble gas activity
— Particulate and iodine activity increased above normal levels indicating some damage may have occurred to the HEPA and possible the charcoal filters
— The temperature in the waste gas storage tanks (upstream of the tested filter) did increase demonstrating that an exothermic reaction did propagate through at least a part of the off gas system.
— A recombiner was installed in the off gas system upstream of the tanks, but is not perfectly efficient.

Investigative Results:

— Silver zeolite can function as a recombiner of H_2 and O_2
— Dehydrated silver zeolite will absorb water until hydrated, which is an exothermic reaction causing the silver zeolite granules to heat up
— During the heating up process, some controlled catalytic recombination may occur further increasing the temperature
— At about 150ºF, the silver zeolite will reach its threshold temperature for H_2 and O_2
— At the threshold temperature, the silver zeolite may cause a rapid recombination (ignition) of H_2 and O_2, if H_2 is above 4% by volume concentration; this may rapidly generate temperatures inside the silver zeolite of 1065ºF

Please refer to a copy of this NRC bulletin in Appendix A.

II. Utilization of Silver Impregnated Zeolites in Radioiodine Air Monitoring Applications

Silver impregnated zeolites have been utilized in monitoring of radioactive iodine's, or removal of radioiodine species in air cleaning systems for many years. The major usage has been in fuel reprocessing facilities such as the Idaho National Engineering Laboratories. The various iodine/iodide species are trapped by adsorption extremely well in the silver zeolite, while the[1] noble gases in the gas stream pass through the zeolite material with very minimal retentions.

The zeolite materials vary in structure; therefore, impregnation of silver onto the zeolite is generally a function of the pore size. The three grades or types of zeolites utilized in the monitoring or cleanup of gas streams containing radioactive iodine species are:

X type =	large pore size
Y type =	medium pore size
Z type =	small pore size

The three grades also differ in their Silicon to Aluminum ration, which primarily determines their acid resistivity properties. Since radioiodine collection efficiency is a function of the silver content and pore size, the X type, which has the greatest pore size and greatest silver content, is the best material to utilize for typical analytical radioiodine monitoring applications that do not involve highly acidic gas streams.

The noble gas retention efficiency of X type Zeolites is $\sim 10^{-6}$ relative to its retention on TEDA impregnated activated charcoal. Since Xenon gas has been utilized to determine this ration, this characteristic has received recognition in the past as the Xenon retention efficiency. It is for this reason that silver impregnated zeolites are utilized in monitoring applications where the gas streams contain both noble gases and radioiodine species. Elimination of noble gas adsorption on the adsorber eliminates the interferences of the Xe-133 Compton background increase in the gamma spectra that obscures the accurate quantitative identification of the I-131 364 HEV peak.

The TMI incident triggered widespread use of silver zeolite cartridges in monitoring applications designed to determine radioiodine concentrations in gas streams or gaseous atmospheres. Silver zeolite cartridges have been utilized extensively in facilities which have fuel cadding leaks that release large amounts of noble gases as well as radioactive iodine species into the reactor coolant, which ultimately reaching other plant systems. Thus, the use of silver zeolite filters has become standard practice in commercial nuclear power plants. Only the cost has kept them from being utilized to a greater extent.

The incident at the LaCrosse BWR facility, involving an explosion during a sampling procedure utilizing silver zeolite cartridge, brought into questions the viability and safety issues regarding the use of silver zeolite materials in an application where hydrogen gas may be present in explosive concentrations. F&J has performed tests on dehydrated and hydrated silver zeolite cartridges to determine temperature increases resulting from introduction of humid air and corresponding values for collection efficiencies for methyl iodide.

III. Temperature Increases and Methyl Iodide Removal Efficiencies of Dehydrated and Hydrated Silver Zeolite Sample Cartridges

The events surrounding the hydrogen gas explosion at the LaCrosse Boiling Water Reactor operated by Dairyland Power Cooperative has caused concern regarding the suitability of utilizing silver zeolite in sampling applications involving gas streams that potentially contain hydrogen gas.

F&J has examined the properties of dehydrated silver zeolite material (<3% moisture) vs. hydrated silver zeolite adsorbent (~10% moisture) with regard to temperature increases vs. time. A gas stream having the following properties was introduced into F&J silver zeolite cartridges having nominal dimensions of 2 ¼” diameter × 1” bed depth:

Flow Rate:	1, 2 and 4 cfm
Relative Humidity:	95%
Temperature:	86ºF
CH_3I Concentration:	1.75 mg/m^3
Test Duration:	CH_3I loading – 2 hours
	Post Sweep – 4 hours

The gas stream containing the radioactive challenge gas (CH_3I) was introduced for a period of two hours. Subsequent to this period the gas stream excluding the challenge gas was passed through the cartridge for a period of 4 hours. The methyl iodide efficiency of the cartridge was measured at each flow rate value for both types of materials utilizing ASTM D3803-Method A type testing.

The following parameters obtained from the test data were tabulated in Table I for each type of material.

A. CH_3I removal efficiency
B. Cartridge water uptake
C. Maximum temperature at cartridge outlet
D. Time to achieve maximum temperature at cartridge outlet
E. Time to return to inlet temperature

The temperature increase at the outlet of the cartridge was measured from time zero to the completion of the test. The methyl iodide efficiency for the hydrated silver zeolite material was greater than the dehydrated material at all flow rates utilized in this test.

A. Graphical representation of the data are as follows:

   Graph II
   The collection efficiency vs. flow rate of hydrated and dehydrated silver zeolite cartridges.

   Graph III
   The temperature increase vs. time for dehydrated silver zeolite cartridges

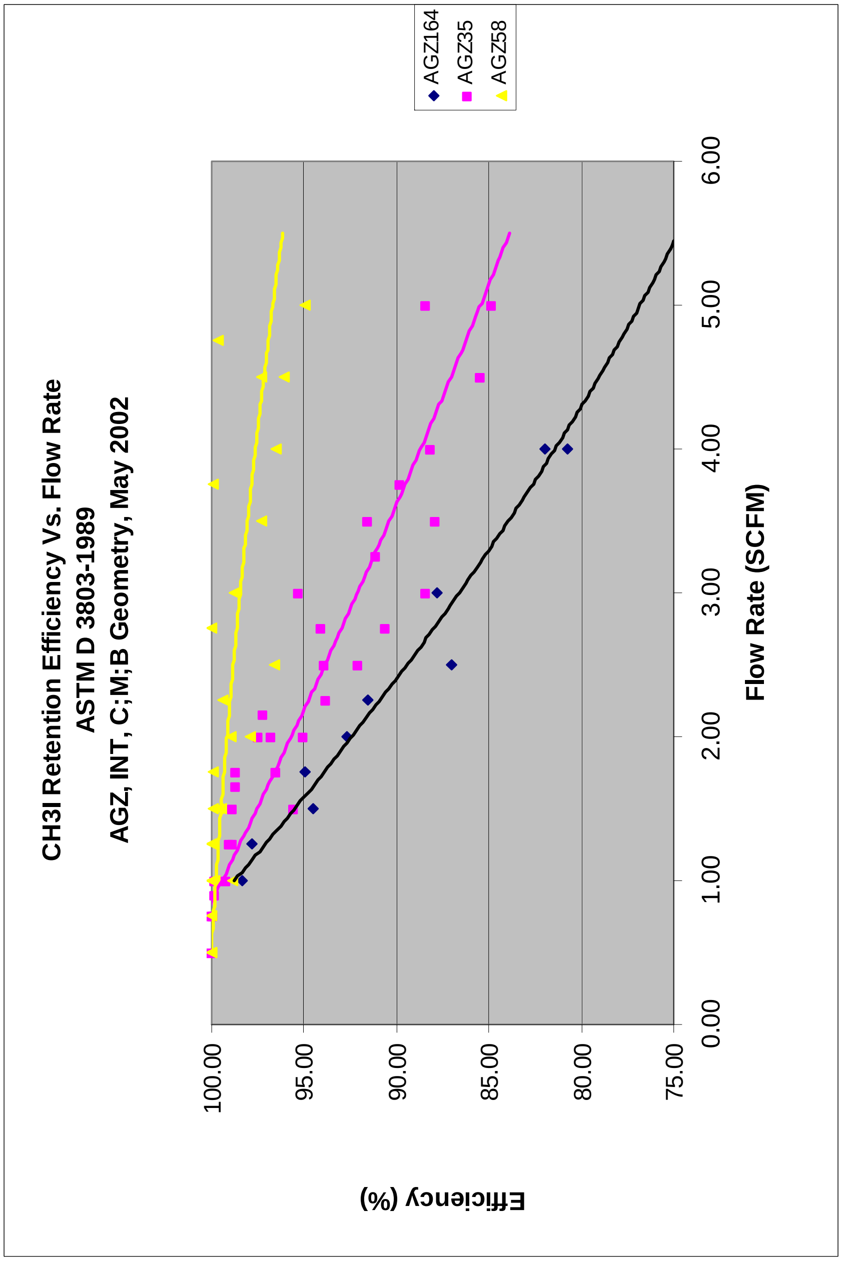
   Graph IV
   The temperature increase vs. time for hydrated silver zeolite cartridges

TABLE I

50 × 80 MESH SILVER ZEOLITE CARTRDIGES

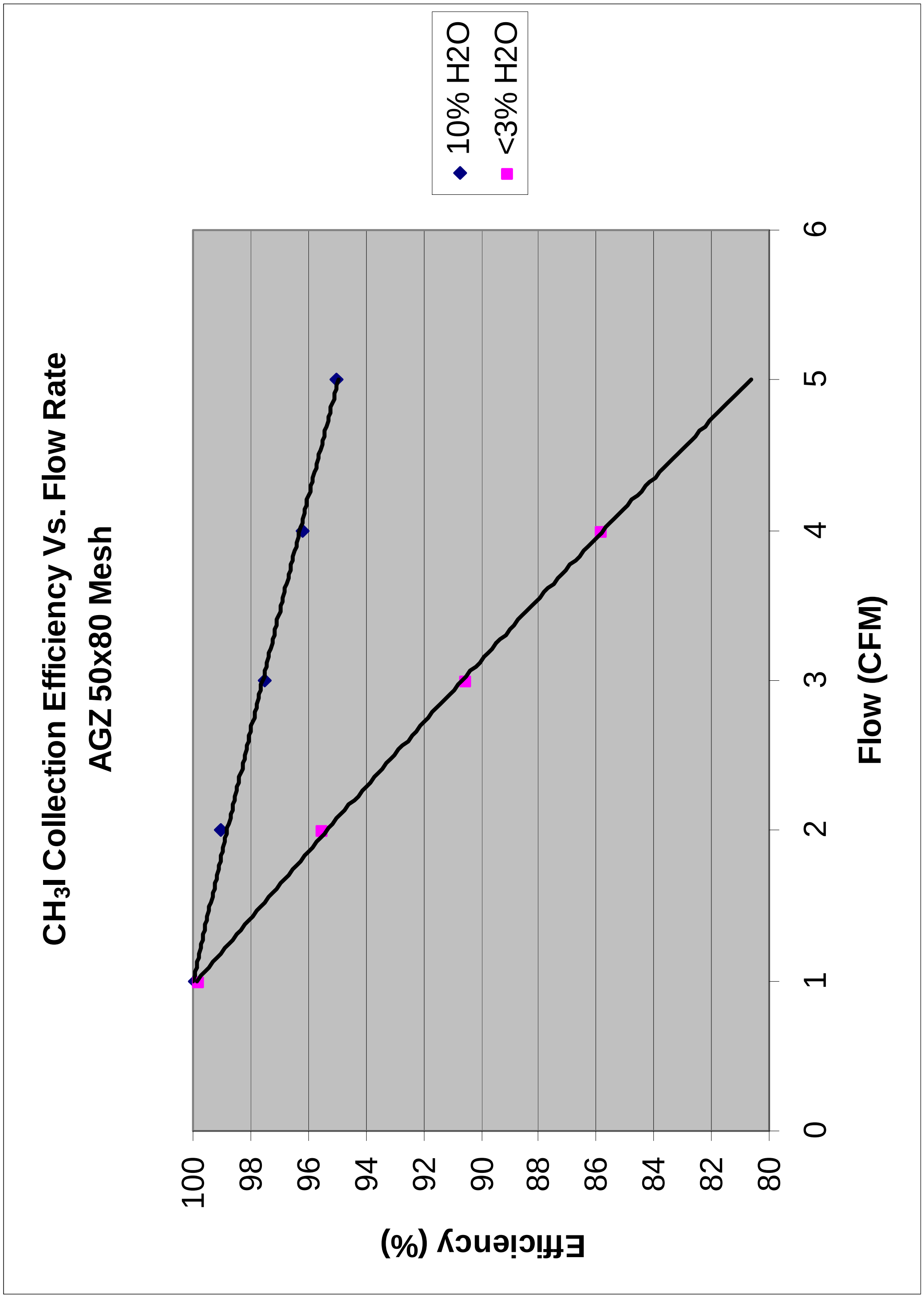
Cartridge Moisture Content	Flow Rate (CFM)	CH_3I Removal Efficiency	Water Uptake	Max Temp. at Cartridge Outlet	Time to Achieve Max. Temp. at Cartridge Outlet	Time to Return to Inlet Temperature
< 3%	1	99.66	8.1 g	192º F	4 min.	50 min.
< 3%	2	95.46	7.0 g	194.5º F	2 min.	30 min.
< 3%	4	85.62	6.6 g	186º F	1 min.	20 min.
10%	1	99.90	2.6 g	93º F	4 min.	60 min.
10%	2	99.43	1.7 g	92º F	2.5 min.	24 min.
10%	4	96.85	1.7 g	94.5º F	1.5 min.	15 min.

Graph I

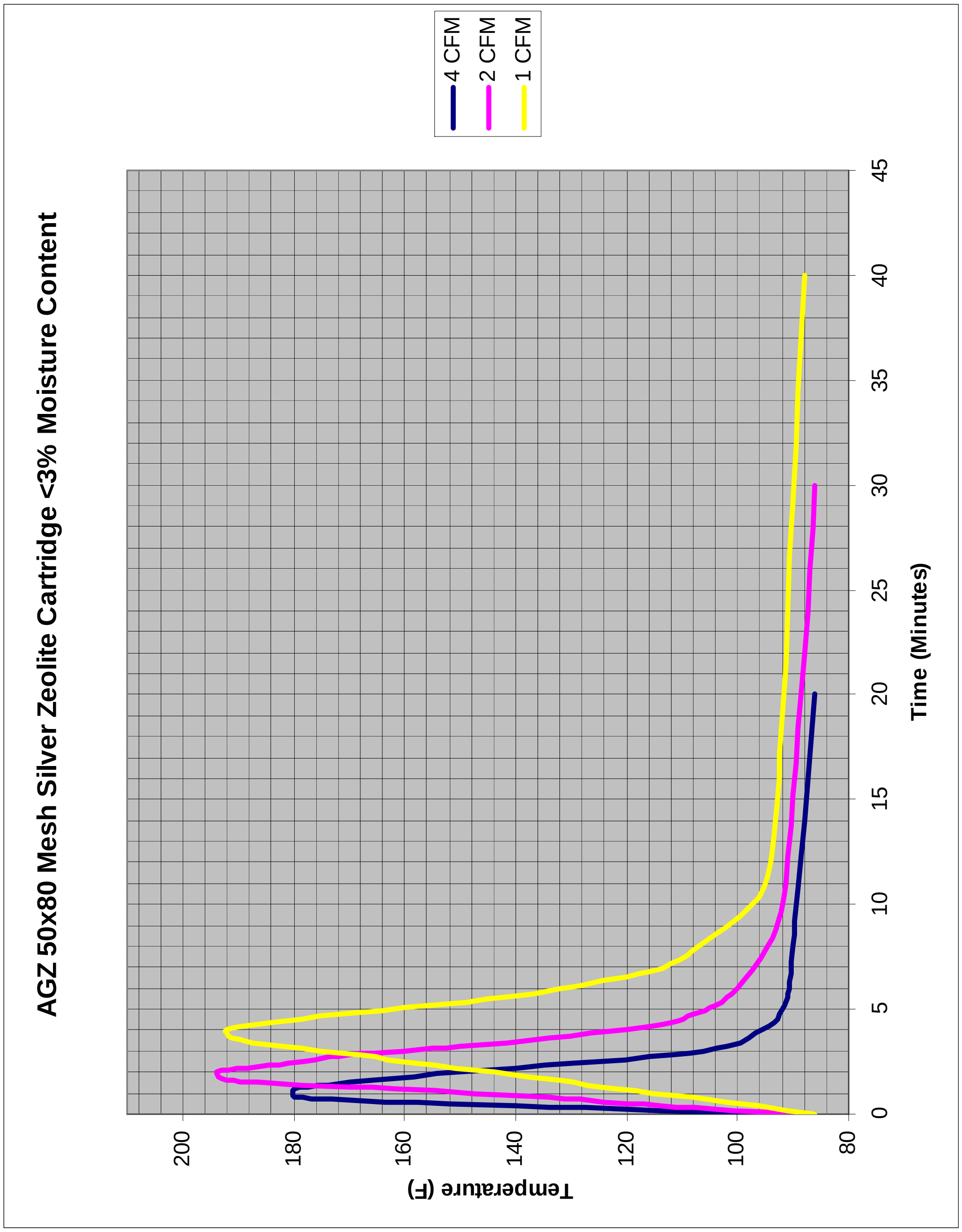


CH3I Retention Efficiency Vs. Flow Rate
ASTM D 3803-1989
AGZ, INT, C;M;B Geometry, May 2002
Efficiency (%)
100.00
95.00
90.00
85.00
80.00
75.00
Flow Rate (SCFM)
0.00
1.00
2.00
3.00
4.00
5.00
6.00
AGZ164
AGZ35
AGZ58

Graph II

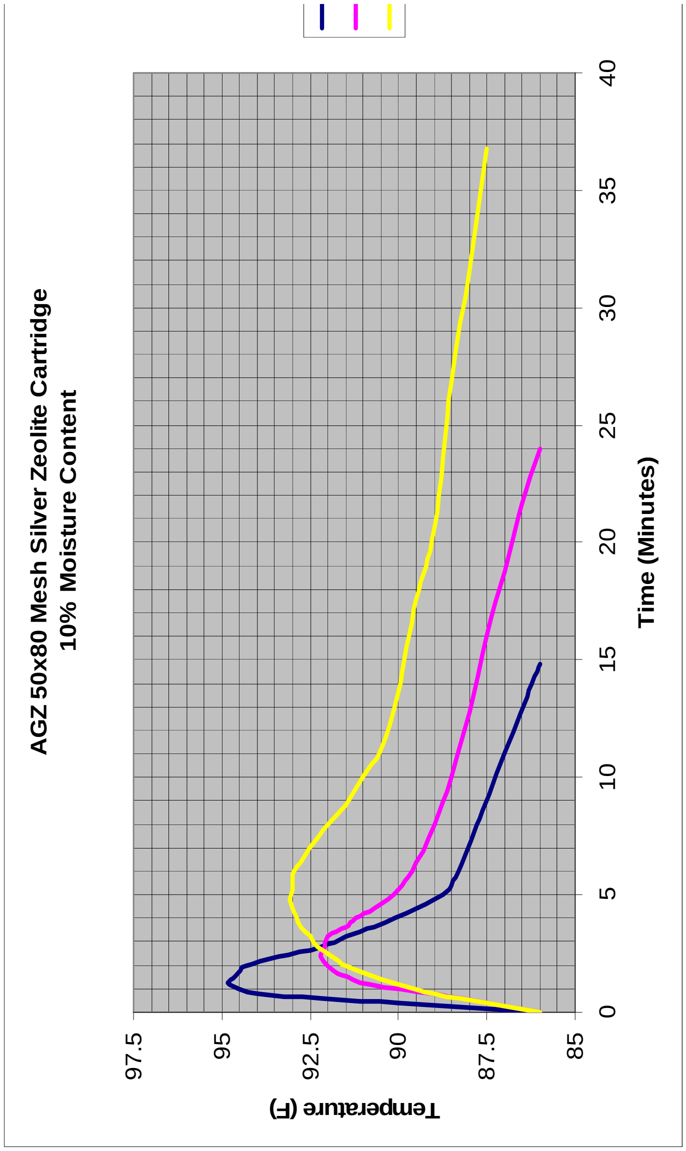

CH_3I Collection Efficiency Vs. Flow Rate
AGZ 50x80 Mesh
Efficiency (%)
100
98
96
94
92
90
88
86
84
82
80
Flow (CFM)
0
1
2
3
4
5
6
10% H2O
<3% H2O

Graph III



AGZ 50x80 Mesh Silver Zeolite Cartridge <3% Moisture Content
4 CFM
2 CFM
1 CFM
Temperature (F)
200
180
160
140
120
100
80
Time (Minutes)
0
5
10
15
20
25
30
35
40
45

Graph IV



AGZ 50x80 Mesh Silver Zeolite Cartridge
10% Moisture Content
Temperature (F)
97.5
95
92.5
90
87.5
85
Time (Minutes)
0
5
10
15
20
25
30
35
40

IV. OBSERVATIONS AND CONCLUSIONS

Observations:

A. The 10% hydrated silver zeolite material has a substantially lower temperature increase at flow rates of 1, 2 and 4 cfm as a result of introduction of humid air through the cartridge than the dehydrated (<3% moisture) material.

B. The temperature increases observed utilizing the hydrated silver zeolite adsorbent (~10% moisture) did not approach the suspected threshold temperature range (150ºF – 275ºF) at which silver zeolite functions as a recombination catalyst for hydrogen and oxygen gas.

C. The temperature increases observed utilizing the dehydrated silver zeolite adsorbent (<3% moisture) exceeded the lower value of the suspected threshold temperature range (150ºF – 275ºF) at which silver zeolite functions as a recombination catalyst for hydrogen and oxygen gas.

D. The methyl iodide efficiency for the hydrated silver zeolite material was greater than the dehydrated material at all flow rates utilized in this test.

Conclusion:

— Hydrated silver zeolite adsorbent media containing approximately 10% moisture by weight is as good as or better a methyl iodide collection medium than the dehydrated material.

— The hydrated silver zeolite product results in temperature increases substantially below the threshold temperature at which silver zeolite exhibits recombination catalytic properties for hydrogen in the presence of oxygen.

— The temperature of the de hydrated silver zeolite media is capable of rising above 150ºF to become a catalyst for the H_2 plus O_2 reaction which further increases the temperature.

— In light of these findings, F&J will continue to provide silver zeolite adsorbent materials containing approximately 10% moisture by weight to all of its customers.

APPENDIX A

OE 1668 GOODMAN (DP&L) 18-MAR-86 06:37 PT
Subject: OFFGAS HYDROGEN EXPLOSION WHILE SAMPLING
Operating Plant Experience Report

UNIT: LACBWR
DOC NO/LER NO: 50-409/NONE
EVENT DATE: 03/06/86
NSSS/A-E: ALLIS CHALMERS/SARGENT AND LUNDY
RATING: 50 MWE
DATE OF COMMERCIAL OPERATION: 11/69
SUPPLEMENTAL DESCRIPTION:

EVENT DESCRIPTION:

Sampling was being performed to determine the efficiency of an offgas charcoal filter. The technique involves drawing offgas from the filter inlet through a sample filter using a vacuum pump and doing the same at the installed filter outlet. Charcoal sample filters had been used previously, but on March 06 Silver Zeolite was being used for the first time in this application to reduce interferences of entrained noble gases. Shortly after starting the sampling pump, the technician noted water drops were accumulating in the Tygon Tubing between the silver zeolite cartridge and the pump. Shortly afterwards, he heard an explosion and saw a blue flash. The explosion occurred 2-4 minutes after sampling commenced. The test rig remained intact and the technician was not injured. He immediately unplugged the sampling pump.

There was a momentary increase in stack noble gas activity. Stack activity then dropped; noble gas activity eventually returned to pre-incident levels, while particulate and iodine activity increased above normal levels, indicating some damage may have occurred to the HEPA and possibly the charcoal filters. The temperature in the waste gas storage tanks, which are upstream of the tested filter, did increase, demonstrating the exothermic reaction did propagate through at least part of the offgas system. There is an installed recombiner in the offgas system, upstream of the tanks, but it is not perfectly efficient.

An investigation into the cause of the offgas explosion was conducted. We found out that zeolite brings down the energy needed for a reaction to occur and that silver zeolite can function as a recombiner. Manufacturers stated that dehydrated silver zeolite would absorb moisture from the sample stream until it reached hydration. During this hydration, which creates a slightly exothermic reaction, the silver zeolite granules will heat up. During this heating, additional hydrogen and oxygen alignment with the silver zeolite molecules may occur and some controlled catalytic recombination may occur. This may further increase the silver zeolite granules' temperature. At about 150ºF, the silver zeolite will reach its threshold temperature for hydrogen and oxygen catalytic recombination. At this threshold temperature, the silver zeolite may cause a rapid recombination (ignition) of hydrogen and oxygen, if the hydrogen is above a 4% concentration. This may rapidly generate temperatures inside the silver zeolite in excess of 1056ºF.

Since the use of the silver zeolite caused the hydrogen explosion, we plan to return to charcoal for this application.

Comments:

This incident introduces a concern over the use of silver zeolite in post-accident sampling applications where hydrogen may be utilized.