Hydrated vs. Dehydrated Silver Zeolite

A Response to an Event at LaCrosse Boiling Water Reactor (BWR) in March 1986 During Air Sampling Activity Utilizing Silver Zeolite

By
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Introduction

The La Crosse Boiling Water Reactor (BWR) event, 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.

Presentation Agenda

- Introduction – LaCrosse BWR event
- Utilization of silver impregnated zeolites in radioiodine air monitoring applications
- Temperature increase and methyl iodide removal efficiencies of dehydrated and hydrated silver zeolite sample cartridges
- Observations and conclusions

Overview

An explosion during a sampling procedure utilizing silver zeolite cartridges brought into question the viability and safety issues regarding the use of silver zeolite materials in an application where hydrogen gas may be present in an explosive concentration.

F&J has performed tests on dehydrated and hydrated silver zeolite cartridges to determine temperature increases resulting from the introduction of humid air and corresponding collection efficiencies for methyl iodide

Vocabulary

- Hydrated Silver Zeolite

  ~10% H_2O

- Dehydrated Silver Zeolite

  <3% H_2O

Background of the LaCrosse BWR Event

The LaCrosse BWR event described in NRC bulletin 50-409

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

Event Observations

- Technician noted water droplets in tygon tubing between silver zeolite cartridge and pump shortly after commencing sampling operations
- There was momentary increase in stack noble gas activity
- Particulate and iodine activity increased above normal levels indicating some damage may have occurred to HEPA and possible charcoal filters

Investigative Results of Event

- Silver zeolite can function as a recombiner of H_2 and O_2
- Dehydrated silver zeolite will adsorb water until hydrated, which is exothermic reaction causing silver zeolite granules to heat up
- During heating up process, some controlled catalytic recombination may occur further increasing the temperature
- At about 150°F, silver zeolite will reach its threshold temperature for H_2 and O_2 recombination reaction
- At threshold temperature, 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 silver zeolite in excess of 1000°F

Utilization of Silver Impregnated Zeolites in Radioiodine Air Monitoring Applications

- Silver impregnated zeolites usages
  - TMI incident triggered widespread use of silver zeolite cartridges in monitoring applications designed to determine radioiodine concentrations in gas streams or gaseous atmosphere containing noble gases
  - Usage includes monitoring of radioactive iodine and removal of radioiodine species in air cleaning systems
  - Used in fuel reprocessing facilities
  - Used extensively in facilities which have fuel cadding leads that release large amounts of noble gases as well as radioactive iodine species into reactor coolant which ultimately reach other plant systems
  - Silver zeolite filters have become standard practice in commercial nuclear power plants
  - Cost has kept filters from being utilized to a greater extent

Utilization of Silver Impregnated Zeolites in Radioiodine Air Monitoring Applications (cont.)

- Zeolite materials structure and grades
  - Three grades of zeolites are utilized in monitoring or clean up of gas streams containing radioactivie iodine species
    - X type – large pore size
    - Y type – medium pore size
    - Z type – small pore size
  - Three grades differ in their silicon to aluminum ratio which determines acid resistivity properties
    - X type has greatest port size and silver content and is best material to utilize for typical analytical radioiodine monitoring applications that do not involve highly acidic gas streams

Utilization of Silver Impregnated Zeolites in Radioiodine Air Monitoring Applications (cont.)

- Zeolite retention properties
  - Noble gas retention efficiency of X type zeolites is 10^{-6} relative to its retention on TEDA impregnated activated charcoal. Since xenon has has been utilized to determine this ratio, this characteristic has received recognition in the past as xenon retention efficiency
  - 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 adsorber eliminates the interferences of the Xe-133 Compton background increase in gamma spectra that obscures the accurate quantitative identification of the I-131 364 keV peak

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

- **Test subjects**

  Dehydrated silver zeolite vs. hydrated silver zeolite

- **Test criteria**

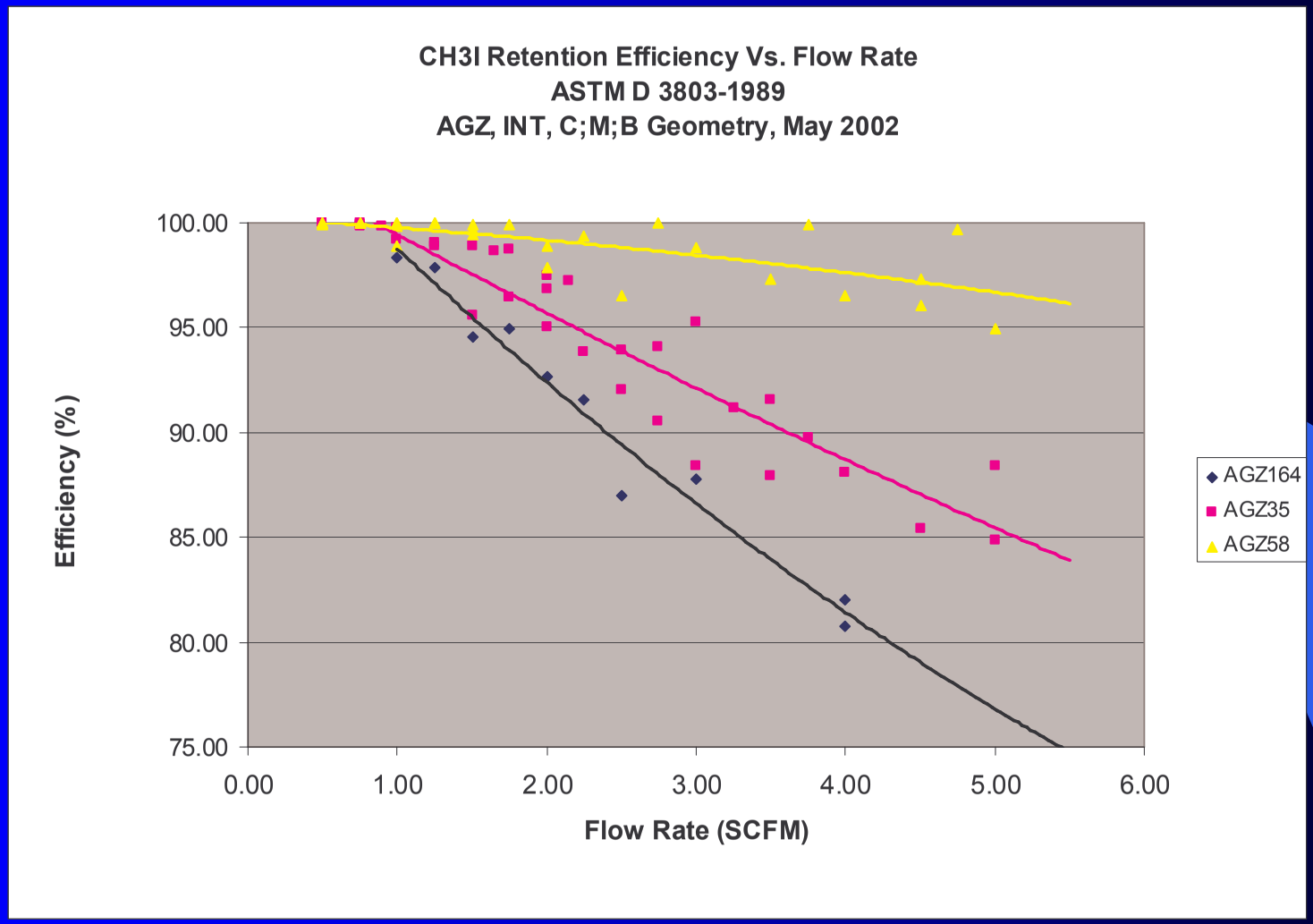
  - Flow rate
  - Relative humidity
  - Temperature
  - CH_3I Concentration
  - Test Duration

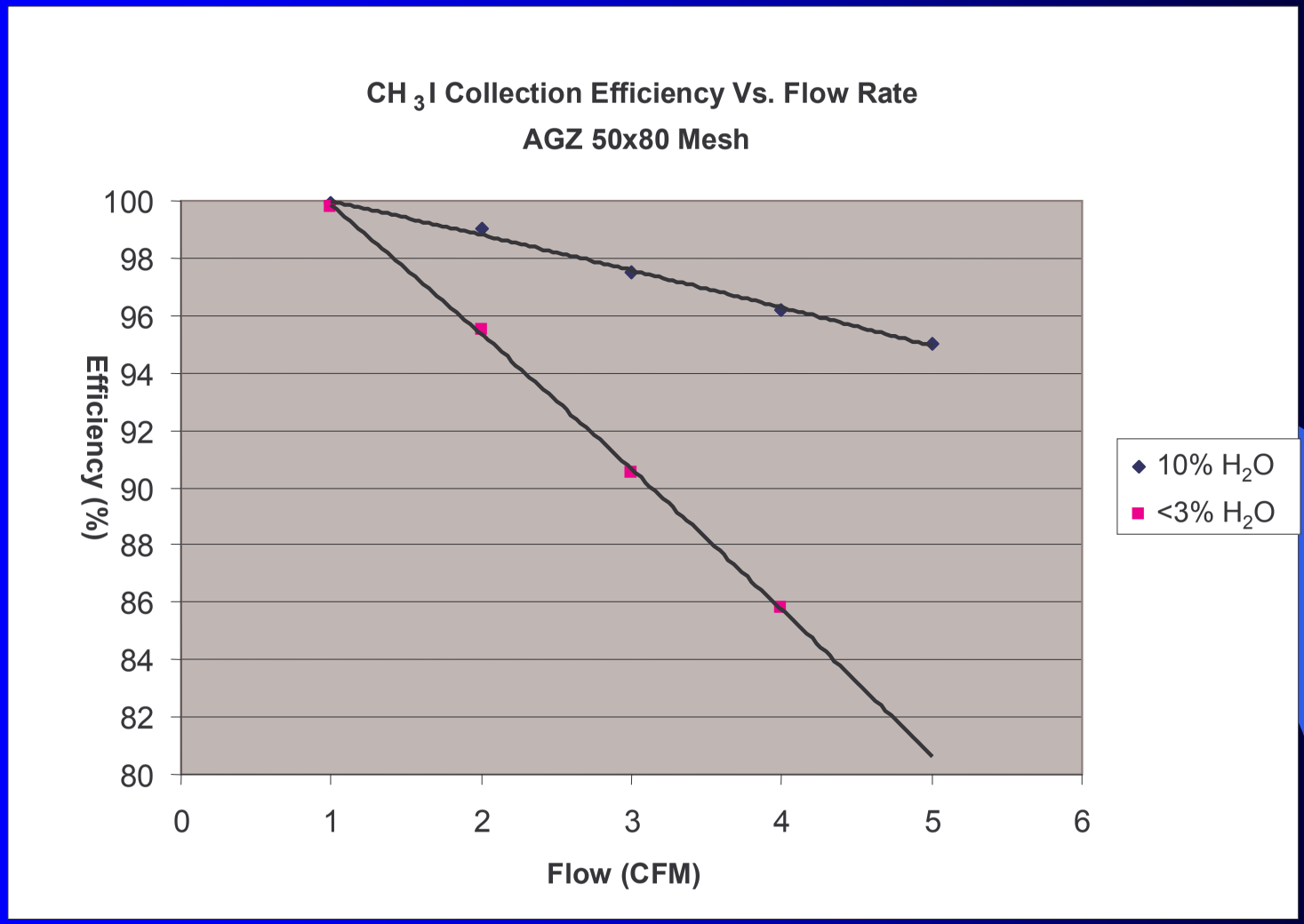
- **Test measurements**

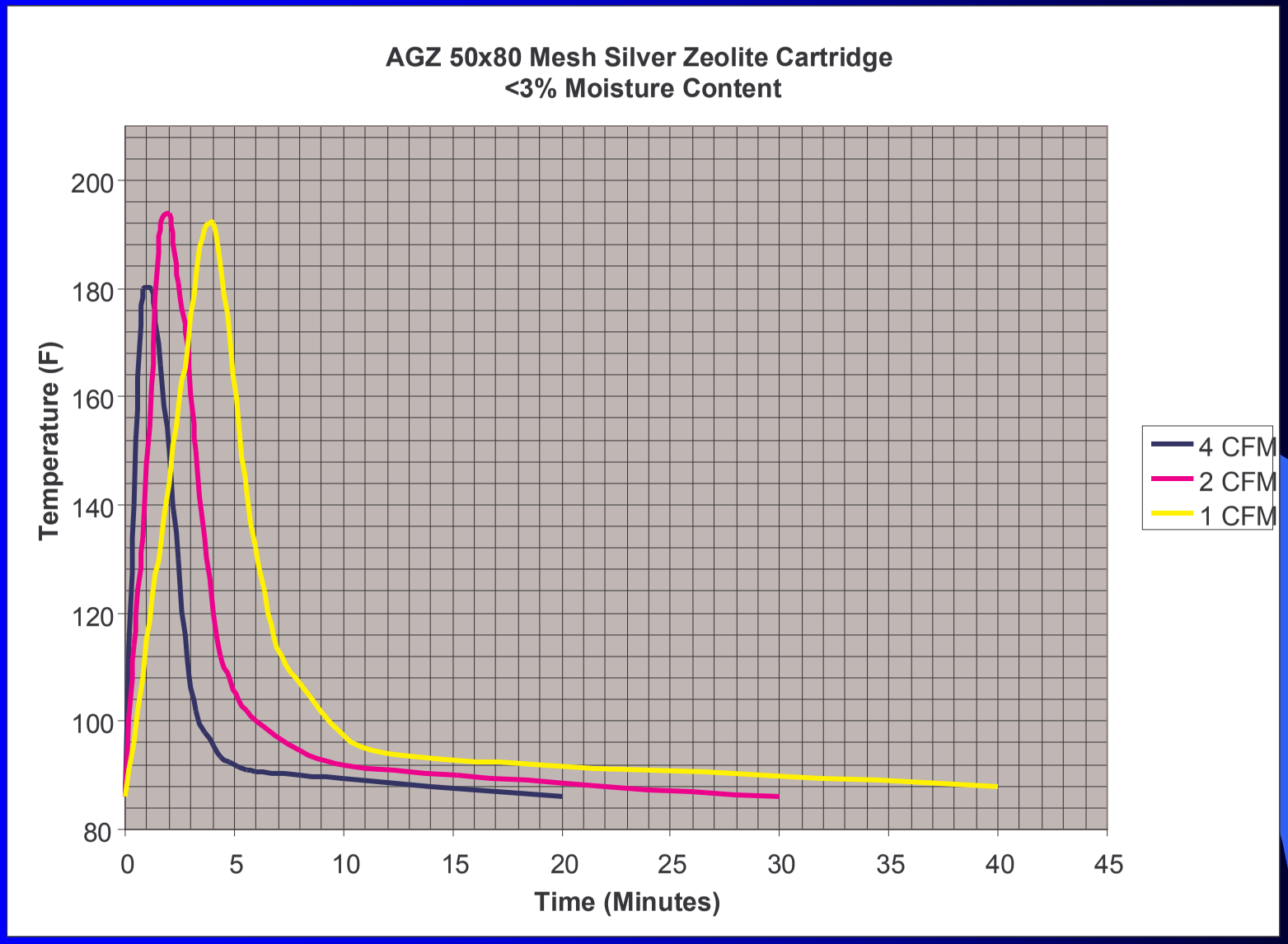
  - CH_3I removal efficiency
  - Cartridge water uptake
  - Maximum temperature at cartridge outlet
  - Time to achieve maximum temperature at outlet
  - Time to return to inlet temperature

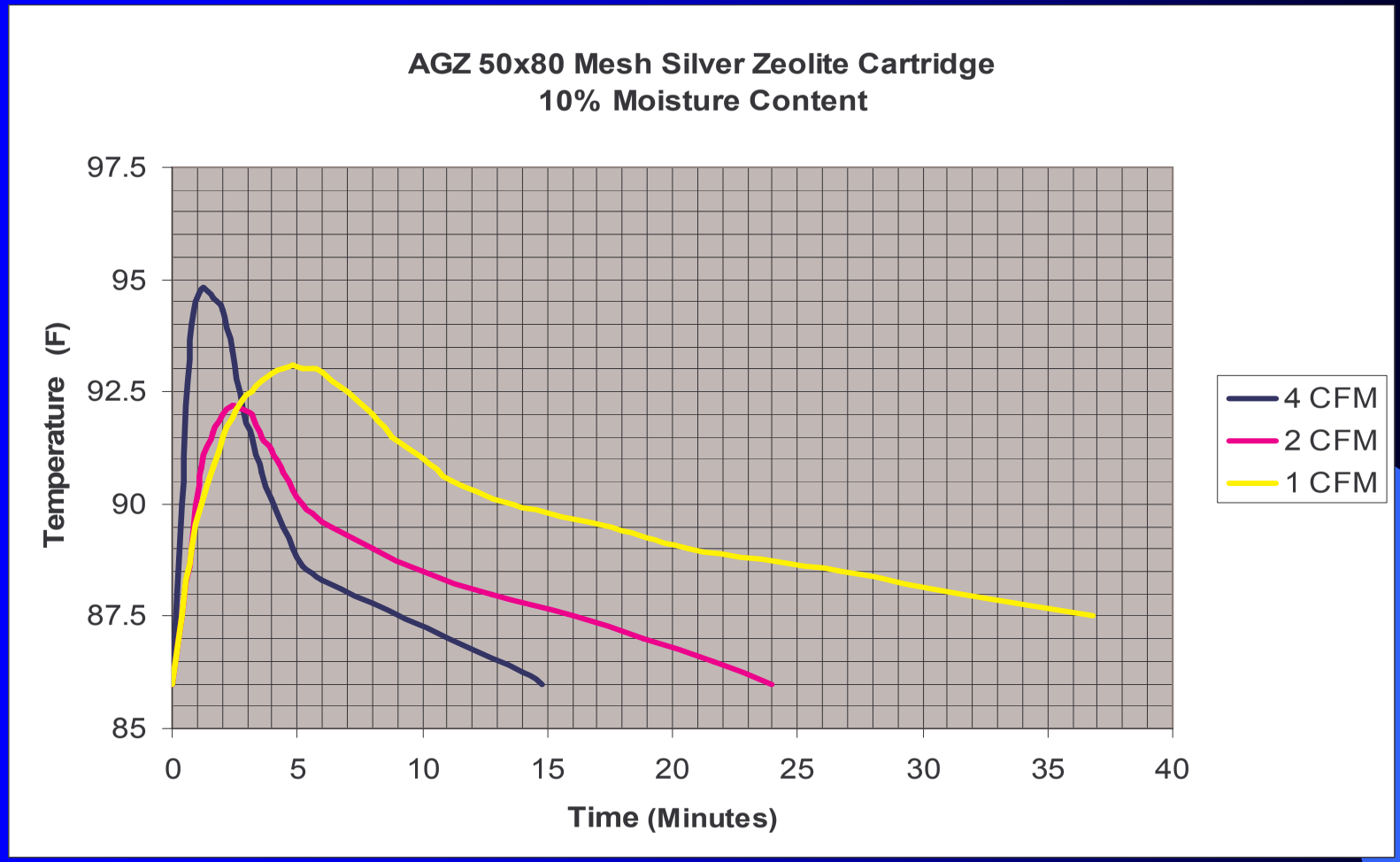
50 x 80 Mesh Silver Zeolite Cartridges

Cartridge Moisture Content	Flow Rate (CFM)	CH_3I Removal Efficiency	Water Uptake	Maximum Temperature at Cartridge Outlet	Time to Achieve Maximum Temperature at Cartridge Outlet	Time to Return to Inlet Temperature
<3%	1	99.66	8.1 g	192°F	4 minutes	50 minutes
<3%	2	95.46	7.0 g	194.5°F	2 minutes	30 minutes
<3%	4	85.62	6.6 g	186°F	1 minute	20 minutes
10%	1	99.90	2.3 g	93°F	4 minutes	60 minutes
10%	2	99.43	1.7 g	92°F	2.5 minutes	24 minutes
10%	4	96.85	1.7 g	94.5°F	1.5 minutes	15 minutes


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
0.00
1.00
2.00
3.00
4.00
5.00
6.00
Flow Rate (SCFM)
AGZ164
AGZ35
AGZ58


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


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


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

Observations

- Hydrated silver zeolite material has lower temperature increase at flow rates of 1,2 and 4 CFM as a result of introduction of humid air through cartridge than dehydrated material
- Temperature increases observed utilizing hydrated silver zeolite adsorbent did not approach suspected threshold temperature (150°F to 275°F) at which silver zeolite can function as a recombination catalyst for hydrogen and oxygen gas
- Temperature increases observed utilizing dehydrated silver zeolite adsorbent exceeded the lower value of suspected threshold temperature range (150°F to 275°F) at which silver zeolite functions as a recombination catalyst for hydrogen and oxygen gas
- Methyl iodide efficiency for the hydrated silver zeolite material was greater than the dehydrated material at all flow rates utilized in this test

Conclusions

- Hydrated silver zeolite adsorbent media containing ~10% moisture by weight is as good as or better a methyl iodide collection medium than the dehydrated material
- 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
- Temperature of dehydrated silver zeolite media is capable of rising above 150°F 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