Pennsylvania Power & Light

Susquehanna Steam Electric Station

Unit 1 Ambient Off-Gas Charcoal System Design Review of Guard Bed Incident of June 13, 1992

June 18, 1992

Introduction

On June 13, 1992, the contents of a component in the off-gas ambient charcoal system ignited while the Unit 1 reactor was in the start-up process. This component, known as the off-gas charcoal system guard bed, is a cylindrical vessel containing activated charcoal.

The purpose of this design review is to focus on the design intent of the guard bed, the purge system utilized for drying the guard bed, and develop a theory of ignition of the guard bed charcoal.

This Design Review represents a team effort, consisting J.E. Agnew, D.G. Kostelnik, D.J. Kohn, R.A. Lengel, and D.J. Morgan, and was performed to support the efforts of the Event Review Team.

General Description

During normal plant operation, process steam from the turbine exhaust is condensed into water in the main condenser. To ensure efficient condensation, the non-condensable gases from radiolysis and air in-leakage are continuously removed by steam-driven ejector nozzles. The gases ejected from the main condenser are then directed through the off-gas treatment system.

The purpose of the off-gas ambient charcoal system is to delay the release of radioactive fission gases to the environment. This allows for most of the Xenon and Krypton activity to decay while in the charcoal thus minimizing activity release. This keeps radiation exposure at the plant site boundary within the limits established by the Code of Federal Regulations and as low as reasonably achievable (ALARA).

The off-gas system consists of two trains, one for Unit 1 and one for Unit 2. Each train consists of two water removal/temperature reduction subtrains, and a charcoal adsorber assembly. The water removal/temperature reduction subtrain consists of a high efficiency particulate air filter (HEPA pre-filter, which is no longer used), a precooler (which is no longer used), a mechanical chiller, and the guard bed. The charcoal adsorber assembly consists of five tanks of activated charcoal, connected in series, and a HEPA after-filter.

Design of the Mechanical Chiller

Off-gas stream water removal is accomplished via the mechanical chiller. It is important that water be removed to prevent excessive water loading of the charcoal adsorber material. The adsorption of fission gases by the charcoal is reduced as the percent of water adsorption is increased, as the charcoal will also adsorb water molecules on the surface of the activated carbon granules. To meet design gas adsorption, the moisture loading must be maintained at ≤5.5%.

The off-gas temperature is reduced to 40°F by the mechanical chiller to remove any moisture in the off-gas stream by reducing its temperature below the dewpoint, condensing the moisture on the refrigerant coil. The off-gas stream is then heated (via a section of heat traced pipe) to lower the relative humidity of the gas, and prevent condensation in the system components. Maintaining the guard bed inlet gas stream temperature (≥65°F DB, ≤45°F WB) will ensure the charcoal moisture content will not be above 5.5%.

Design of Guard Bed

The guard bed consists of a cylindrical vessel, approximately 9 feet high and 30 inches in diameter. The guard bed is filled with approximately 1280 pounds of activated charcoal.

The guard bed serves two basic functions:

- remove iodine that may be entrained in the off-gas stream
- act as a sacrificial filter and adsorb excessive water vapor that may be in the off-gas stream as a result of failure or malfunction of the mechanical chiller.

It is important to note that the guard bed is intended to adsorb moisture in the form of water vapor in the off-gas stream. It is not intended to absorb water in the liquid state.

Moisture detectors are installed on the inlet and outlet of the guard bed to detect the presence of moisture entering the guard bed, and to monitor guard bed performance approaching saturation conditions.

Information supplied by the manufacturer (in IOM #424) indicates that liquid water introduction into the guard bed is sufficient cause to switch operation to the alternate off-gas treatment subtrain.

Design of Purge Skid

A low pressure system is provided to regenerate (dry) the guard bed charcoal, should it adsorb water vapor in excess of 5.5% by weight. This system consists of an air compressor, and a heater to assist in drying.

The purge system is intended to be operated when the mechanical chiller has failed. The purge system will effectively remove adsorbed water vapor, but is ineffective in removing liquid water, or drying wetted charcoal. Thus, it should not be used if the presence of liquid water is suggested.

Information supplied by the manufacturer suggests that "excessive wetting" occurs when the normal guard bed pressure differential (approximately 2" water gauge) has doubled. By this criteria, purging should only be considered if:

- the mechanical chiller has failed <u>and</u>
- the current guard bed differential pressure has <u>not</u> increased to twice its normal value. (For example, if the dry guard bed differential pressure at normal off-gas flow rate is 2" water gauge, doubling this differential to 4" indicates the presence of liquid water. For other off-gas flow rates, it will be necessary to determine the associated dry guard bed differential pressure.)

Effect of Wetting Guard Bed Charcoal

Wetting of charcoal will have several effects, not all of which are well understood.

Charcoal, when wet and subsequently dried, will undergo an embrittlement process, and fracture into smaller particles, thereby increasing the total charcoal surface area.

The process of wetting and drying of organic materials, by nature, will tend to produce heat and elevate the internal temperature, and is the main cause of spontaneous combustion.

Activated charcoal, when manufactured, has a relatively low moisture content, and undergoes a controlled process by the manufacturer to bring the charcoal to equilibrium prior to packaging and shipping. During this time, the material is susceptible to spontaneous combustion.

Theory of Ignition

Spontaneous combustion, by itself, is not a well understood process.

Any combustion process requires three things: oxygen, fuel source, and heat. Charcoal, by nature, will adsorb elemental oxygen, and react with it at a rate dependent on temperature and charcoal conditions.

Under no-flow conditions, the physical configuration of the guard bed vessel will tend to increase the potential for spontaneous combustion. It is estimated that the spontaneous combustion temperature, given the existing configuration, is in the range of 125°F to 150°F. (Refer to the attached Spontaneous Combustion of Charcoal Theory.)

The process of wetting charcoal, by nature, will tend to produce heat and elevate the internal temperature. Drying may increase the chemical activity, or rate of oxidation, and will raise bed temperature due to contact with warm air. All these increase the potential for spontaneous combustion.

Activated charcoal, when manufactured, has a relatively low moisture content, and undergoes a controlled process by the manufacturer to bring the charcoal to equilibrium prior to packaging and shipping. Per the manufacturer, this is to reduce the potential for spontaneous combustion while packaged in closed containers.

The activated charcoal, by nature, will adsorb oxygen, and will subsequently oxidize. This process occurs at room temperature and releases heat. This will increase the temperature of the charcoal, which will increase the rate of reaction. If heat cannot be removed rapidly enough, a runaway temperature rise will occur that will ignite the charcoal.

The presence of water will aggravate the situation, altering the charcoal physical structure by opening new sites for oxidation.

Repeated wetting and drying of the activated charcoal may tend to reduce the temperature at which spontaneous combustion occurs.

Flooded charcoal will not ignite; however, that area just above the water line may be more prone to spontaneous combustion.

The action of heated air purge may increase the combustion potential by adding both heat and oxygen to the fuel source.

Recommendations

Recommendations by the Design Review Team have been incorporated into Section VI of the Event Review Team Report.

SPONTANEOUS COMBUSTION OF CHARCOAL THEORY

BY Don Kohn
June 17,1992

I. BACKGROUND INFORMATION ON SPONTANEOUS COMBUSTION

A. Factory Mutual Data Sheet 8-10 "Coal and Charcoal Storage"

1. Charcoal has a tendency to spontaneous heat when fresh or wet.
2. Smaller size charcoal results in greater hazard.
3. Thoroughly dried pulverized charcoal has a definite explosion hazard. With sufficient lapse of time for charcoal powder to absorb moisture form normal atmosphere, the explosion hazard is considerably reduced.
4. Ventilation of bulk storage of charcoal (as in silos) should be from above. Flow up through the material may cause spontaneous heating.
5. During a fire in wet charcoal; carbon monoxide, carbon dioxide, steam and hydrogen may be formed.

B. Factory Mutual Data Sheet 7-2 "Waste Solvent Recovery"

The chemical industry uses charcoal bed adsorption beds similar to SSES off-gas systems guard bed to recover solvents. While the process is more dangerous due to the flammable solvents and the solvents will lower the charcoal ignition temperatures, the information is useful.

1. Most charcoal beds develop background level of 2000-3000ppm of CO. An alarm point that indicates combustion should be 50-100% above background.
2. To minimize spontaneous heating during the desorption (done with steam) phase maintain at least 75% of the normal airflow through the carbon bed when not steaming and program the drying/cooling phase so that the carbon remains wet.
3. During extended shutdowns, the airflow should be maintained at 75% of the normal airflow, and the bed should not be allowed to dry out. If nitrogen or carbon dioxide is used to inert the bed, oxygen levels inside the unit, including the void spaces in the beds, should not exceed 1% by volume.
4. Adsorbers should be designed for even air distribution. Dead spots will increase the probability of spontaneous heating.

C. Ignition Temperature Investigation of Off-Gas from SSES, NUCON May 21, 1987

1. At 360 °F, there is sufficient temperature to start oxidation.
2. Ignition temperatures at different air flows were 360-470 °C (680-878 °F).

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1. If the charcoal was purged to a very dry state, adsorption of water vapor (heat of adsorption) would account for 10 cal/g or a total of 2.3 x 10^4 BTU. (note: If dry air continued, then the heat of adsorption of oxygen and the heat of oxidation may both be possible.

E. PP&L's IOM 424-1

1. Section 2.1.3.1 The guard beds ability to adsorb water in the event of a total chiller failure is based on the charcoal's ability to adsorb water of 40% of its dry weight. (This implies that standing water is not expected nor designed for).
2. Section 4.4 (page 92) There is a warning that if there is a chiller failure and a high chiller level alarm, a possibility of carrying liquid droplets to the guard bed exists.
3. Section 4.4 (page 93) "If a high chiller drain pot alarm (LAHH-17135A) occurs in conjunction with the moisture alarm or alone, subtrain transfer should be made immediately since water carryover into the guard bed will otherwise occur."
4. Section 4.4 (page 94) "While sufficient operating experience has not as yet been accumulated, it is suspected that repeated saturation and thermal cycling would be increased dust formation." (Increased dust would allow increased oxidation and increased absorption of water which both produce heat.

F. Fire Protection Handbook (16th Edition)

1. Page 5-64 Under certain conditions, charcoal reacts with air at a sufficient rate to cause the charcoal to heat spontaneously and ignite. Among the principle causes of spontaneous heating is charcoal becoming wet and friction in grinding of charcoal into finer sizes. (Dusting due to wet charcoal being dried could be similar to grinding.)
2. Table 5-11J (Page 5-130) Charcoal has a high tendency for spontaneous heating. The material should be kept dry and ventilated. Avoid wetting and subsequent drying.
3. Page 11-52 "... wet charcoal is even more susceptible to self-heating than when dry." (It is not clear if the hazard exists with the charcoal in the wet state or after the wet charcoal dries.
4. Page 12-36 Charcoal is somewhat unique. Most materials must be heated to produce gases which can then chemically react with oxygen to "burn". Charcoal can directly (in the solid state) combine with oxygen as evidenced by glowing and the absence of flames.

II. SPONTANEOUS COMBUSTION THEORY

A. Spontaneous combustion occurs when heat is generated faster than the heat can be removed resulting in an increase rate if temperature rise which will raise the material to its ignition temperature. Spontaneous heating in charcoal is a complex event. Heat generation in the guard beds can be a result of adsorption of oxygen and water, oxidation of the charcoal and/or decay of adsorbed radioactive materials.

B. Spontaneous combustion is known to occur with charcoal. New freshly manufactured charcoal which has not been allowed to reach equilibrium with the moisture and oxygen in the surrounding air is very prone to spontaneous combustion. Dry charcoal appears to be the most resistant to spontaneous combustion. Wet charcoal is described as more prone to spontaneous combustion, but it is not clear if the wet charcoal is the problem or the problem starts when the wet charcoal drys out. Clearly warnings exist to prevent wetting and to take care with the subsequent handling of wet charcoal.

C. The SFPE Handbook of Fire Protection Engineering Section 1/Chapter 22 discusses self heating and spontaneous combustion. Different physical storage arrangements will have different abilities to dissipate the heat that is generated by materials subject to spontaneous combustion. A methodology is provided to determine, for a specific physical arrangement and a specific temperature of the material, if the conditions are favorable for spontaneous combustion. If critical conditions exist, then spontaneous combustion is possible but the time factor can not be determined with out specific heat release rates. It also indicates that when the temperature is below the critical point, spontaneous combustion will not occur.

Using the methodology, for a specific physical arrangement and temperature, Sigma can be calculated and compared to Sigma-critical. When Sigma is equal or above Sigma-critical the conditions are favorable for spontaneous combustion. When Factory Mutual performed an ASTM E-771-81 test in 1987 with new moist (only adsorbed water) charcoal, it did not spontaneously heat when exposed for 24 hours to a temperature of 405 °F. In the attached Spread sheet, Case #2 calculates Sigma for a configuration such as the ASTM apparatus using data (C_1 and C_2) available for a non-charcoal material. The specific data for the charcoal used in the guard bed is not currently available to perform these calculations. The results of Case #2 indicates that conditions in the ASTM test apparatus would be ideal for spontaneous combustion above 375 °F. Case #1 calculates Sigma for the guard bed configuration also using data for the non-charcoal material. The results indicate that the corresponding critical temperature to initiate spontaneous combustion is above 125 °F. While we do not know the actual data for charcoal required to calculate Sigma, the Factory Mutual test results indicate that the actual charcoal data would result in higher critical temperatures and therefore suggests 125 °F as an upper limit to bed temperatures required to prevent spontaneous combustion in moist charcoal. If the critical temperature for spontaneous combustion is conservatively assumed to be 700 °F (The ignition temperature range) then at that temperature Sigma would equal Sigma/critical in the ASTM apparatus. By making conservative assumptions and solving for the variables C_1 and C_2, we can calculate a Sigma for the guard bed configuration. The result is about 300 °F which suggests that with moist charcoal in the guard bed conditions would be favorable for spontaneous combustion at a temperature between 125 and 300 °F. Since wet (or wet then dried) charcoal is more prone to spontaneous combustion, the critical temperatures may be less. This suggests that conditions were favorable in the 1B guard bed for spontaneous combustion.

D. There is insufficient data at this time to calculate the time required for spontaneous combustion. However, the time required for spontaneous combustion relies on at least three parameters:

1. The temperature difference between the charcoal and the charcoal ignition temperature. Lowering of ignition temperature via contaminates will shorten the time. Higher bed temperatures will also shorten the times.

2. The rate of heat generation. Both oxidation and moisture adsorption produce heat. The condition of the charcoal dictates the oxidation and adsorption rates and therefore the heat generation rates. Wet charcoal and/or dried charcoal may have higher heat generation rates than charcoal which has reached equilibrium with the atmosphere.

3. The heat capacity is also a factor. Due to the moisture, wet charcoal will heat up slower than dry charcoal.

III. CONCLUSIONS

A. The charcoal was wet (liquid water) based on the drying times and the water found in the 1A Guard bed. The subsequent drying with very dry air created charcoal very prone to spontaneous combustion.

B. The geometry of the guard bed suggests that conditions would be favorable for spontaneous combustion at temperatures as low as 125-150 °F. The guard bed temperature after the confidence purge was measure at 135 °F.

C. The time required for the self-heating conditions to reach ignition temperature can not be calculated with the existing data. It seems probable that the time was short since the charcoal was in a very susceptible condition for self-heating. (Also there may have been bed temperatures higher than those recorded.)

D. Laboratory testing with new charcoal (and maybe the used charcoal) can be conducted to determine the time duration required to obtain spontaneous combustion with wet then dried charcoal under no or limited flow conditions.

CASE #1

r=	15.00	inches	l=	9.000	feet
r=	0.381	meters	l=	2.743	meters

T (deg F)	Tr (K)	SIGMA*	SIGMAc **
50	283.0	0.048	2.065
75	296.9	0.175	2.065
100	310.8	0.566	2.065
125	324.7	1.648	2.065
150	338.6	4.383	2.065
175	352.4	10.756	2.065
200	366.3	24.587	2.065
225	380.2	52.762	2.065
250	394.1	107.015	2.065
275	408.0	206.355	2.065
300	421.9	380.220	2.065
325	435.8	672.395	2.065
350	449.7	1145.683	2.065

CASE #2

r=	12.500	mm	l=	25.000	mm
r=	0.0125	meters	l=	0.0250	meters

T (deg F)	Tr (K)	SIGMA*	SIGMAc **
325	435.8	0.724	2.841
350	449.7	1.233	2.841
375	463.6	2.031	2.841
400	477.4	3.245	2.841
425	491.3	5.039	2.841
450	505.2	7.628	2.841
475	519.1	11.275	2.841
500	533.0	16.308	2.841

*SIGMA = (C1) * [(r^2) / (Tr^2)] * [EXP(C2 / Tr)]

**SIGMAc = 2.00 + (0.841) * [(r^2) / {(0.5 * l)^2}]

For Animal Feedstuff:

C1 = 2.088e+17

C2 = -8404