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ENGINEERING DESIGN OF THE PDF & XPD BEAMLINE SAMPLE ENVIRONMENT FOR SAFE EXPERIMENTAL USE OF HAZARDOUS GASES

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Abstract

The Pair Distribution Function (PDF) and X-ray Powder Diffraction (XPD) beamlines located at the 28-ID at Brookhaven National Laboratory's (BNL) National Synchrotron Light Source II (NSLS-II) require a means for safely supplying, containing, and exhausting hazardous gases to and from experimental samples. The PDF/XPD sample environment includes a sample holder, internal beam stop, sample chamber, and stages that provide eight degrees of freedom. A specially-designed window is also included for maximum X-ray transmission at minimum cost. Sensors, flow metering devices, and circuitry are included to provide proper purging, control hazardous and dilution gas flows, and integrate the safeguards needed for safe operation.

INTRODUCTION

The PDF and XPD beamlines collect X-ray pair distribution function and diffraction data from samples using high energy (i.e. > 25 keV) X-rays. A specially-designed Gas Handling System (GHS, see Acknowledgments) supplies a variety of hazardous and non-hazardous gases to an outlet port for in-situ and in-operando studies of chemical reactions. A specially-designed sample environment is needed to contain and supply gases to experimental samples, position samples quickly, accurately, and remotely, collect scattered X-rays over a wide-angle without distortion, dilute hazardous gases after flowing through the samples, and then safely exhaust the gas mixtures. Excluding inert and non-reactive gases, the GHS supplies hydrogen, methane, ethylene, oxygen, carbon monoxide, NO_x, SO_x, and CH_3S_x (e.g. methyl mercaptan and methional) gases and mixtures.

SAMPLE ENVIRONMENT DESIGN

The sample environment includes: a sample chamber, a sample holder and sample, an internal beam stop, and stages to remotely position the sample, sample chamber, and beam stop. The samples are contained in capillary tubes and retained by miniature collets in a holder designed to allow gases to pass through the samples. The sample chamber is vented externally and inert gas dilutes hazardous gases after flowing past each sample. Seals and materials are compatible with the gases used, and the sample chamber has windows to cost-effectively allow entrance of a .5 mm x .5 mm X-ray photon beam and undistorted exit of scattered X-rays over a wide (± 30°) angle from the sample center. Lastly, the sample environment requires similar protections and safety provisions as the GHS. Two cameras, a goniometer, and X, Y, and Z stages are used to align the capillary tubes. Once aligned, electrical power is disconnected for safe operation when using flammable gases. The sample chamber is large enough to contain a goniometer and an internal beam stop (to prevent X-ray scatter from the downstream window) yet small enough for ± 30° unobscured collection of scattered X-rays. An image of the sample environment is shown in Figure 1.

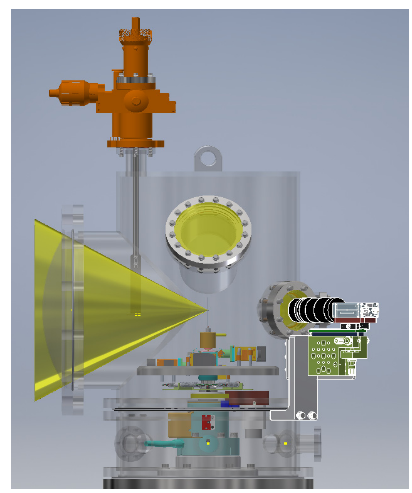

Figure 1: Sample environment with transparent sample chamber and ± 30° scattered X-ray exit cone.

The X-ray sample chamber is composed of two sections, the upper section has an upstream Be window for monochromatic photon beam input, a large port downstream to collect scattered X-ray data, an internal beam stop (with remote X and Y stages), two camera ports, and a view port. It connects to a lower spool section which contains the feedthroughs for gas inputs, exhaust, sensors, electrical power, and controls. The upper section can be removed quickly for non-hazardous gas experimental use.

To meet BNL safety requirements, the sample chamber materials must be compatible with all gases used and the chamber must withstand 1 atmosphere external pressure (and internal vacuum for leak-check verification) with a safety factor of 3.0 on yield stress. The chamber wall thicknesses were determined by iterative finite element analysis (FEA) modeling using standard material stock sizes. Since all gases used are compatible with stainless steel, 304/304L stainless steel

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was selected to keep costs low and 304L material properties were conservatively used to allow chamber fabrication from either 304 or 304L since 304 has a higher yield strength than 304L. Figure 2 shows the maximum Von Mises stress of 11.05 ksi. This provides a 3.17 safety factor with a material yield stress of 35 ksi.

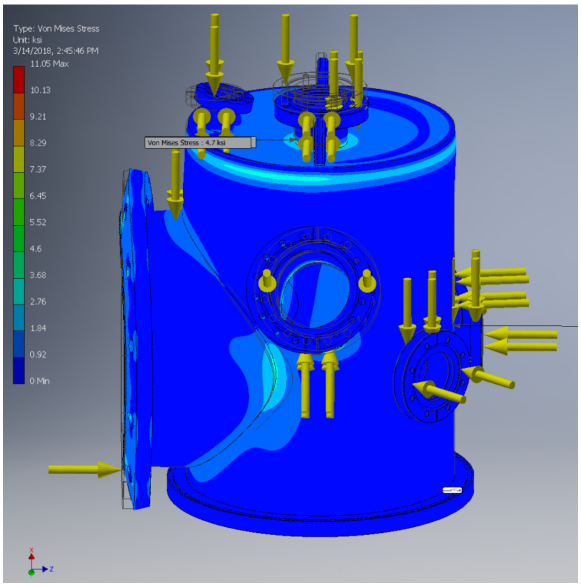

Figure 2: Sample chamber FEA.

The downstream window of the sample chamber presented an interesting challenge. Since the detector could not be placed in the same chamber as the reactive gases, an external window was required. Using a detector of fixed size to collect scattered X-rays at ±30°, the downstream window had to be located at close as practical to the sample center to minimize the chamber size and window thickness. This maximizes scattered x-ray transmission. Many window materials and numerous designs were considered and rejected. The window design chosen is a domed aluminum window, TiN coated to minimize aluminum/gas reactions. For similar reasons, annealed nickel was chosen for the metal gaskets.

A major advantage of using aluminum for the exit window material is the ability to machine a domed window with the center of the dome at the center of the sample. The domed shape provides a thinner window than flat windows of the same material since the external pressure loads are resisted by membrane instead of bending stresses. Numerous FEA runs were undertaken to minimize the wall thickness within the ±30° scattered X-ray exit cone and results from two FEA programs were compared for validation. A wall thickness of 1.5 mm was selected even though FEA results showed a thinner dome can withstand the pressure differential; manufacturing and handling concerns led to the 1.5 mm wall thickness selection. Figure 3 shows FEA results and X-ray transmission data for three window materials. The maximum stresses of 2.54 and 2.67 ksi from Inventor and ANSYS respectively provide a safety factor > 13 and agree reasonably well.

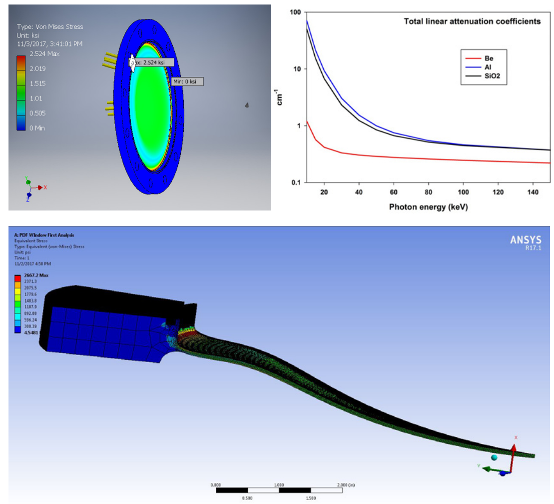

Figure 3: X-ray exit window (a) Inventor FEA, (b) transmission data for Be, Al, and fused silica materials, and (c) ANSYS FEA.

Elimination of Hazard

The PDF and XPD hazardous gases are toxic, flammable, explosive, or a combination of the first two. NSLS-II requires hazard mitigation by first substituting less hazardous alternatives, by using engineering then administrative controls, and lastly by using personal protective equipment. The method selected for PDF and XPD is to eliminate the hazard by diluting hazardous gas emitted from the capillary tube with an inert gas flowing at a sufficient rate to produce an effluent safe enough for breathing. Fluid flow calculations provided the maximum practical dilution gas flow rate. This flow rate in turn set the allowable maximum flow rate for each hazardous gas. Numerous U.S. resources were used to obtain the required dilution quantities. In the tables below for each gas, the Recommended Exposure Limit (REL) is published by the National Institute for Occupational Safety and Health (NIOSH), and the Permissible Exposure Limit (PEL) is published by

the Occupational Safety and Health Administration (OSHA). The Threshold Limit Value (TLV) is published by The American Conference of Government Industrial Hygienists (ACGIH), and the Lethal Concentration fatal to 50% of test subjects (“LC_{50} dose”) were obtained from Safety Data Sheets for each gas. These resources also provided the Lower Flammability Limit (LFL) and the Lower Explosive Limit (LEL) for flammable and explosive gases. For flammable gases, the lesser of the LFL or LEL/4 is required. For toxic gases, BNL requires LC_{50} dose/100 for gas effluent. The safest of all the above values was used for gas dilution. This is shown in Table 1 and Table 2 below.

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Table 1: Flammable and Explosive Gas Dilutions

Gas	LFL/LEL (% volume of air)	Gas Flow (SCFM inert, ml/min Haz)
Hydrogen (H_2)	4 / 18.3	0.042 @ 50 ml/min
Methane (CH_4)	5 / -	0.034 @ 50 ml/min
Ethylene (C_2H_4)	2.7 / -	10 @ 50 ml/min
Methional (CH_3SCH)	3.9 / -	10 @ 3.6 ml/min

Table 2: Toxic Gas Dilutions

Gas	REL\PEL (PPM)	TLV (PPM)	$LC_{50}/100$ (PPM)	Gas Flow (SCFM inert, ml/min Haz)
Carbon Monoxide (CO)	35 \ 50	25 TWA	37.6	10 @ 7 ml/min
Nitric Oxide (NO)	25 \ 25	25 TWA	1.15	10 @ 0.3 ml/min
Nitrogen Dioxide (NO_2)	1 \ 5	0.2 TWA	1.15	10 @ 0.06 ml/min
Sulfur Dioxide (SO_2)	2 \ 5	.25 STEL	25.2	10 @ 0.07 ml/min
Ethylene (C_2H_4)	200 \ Not Found	200 TWA	Not Found	10 @ 57 ml/min
Methional (CH_3SCH)	Not found	Not found	12.67	10 @ 3.6 ml/min
Methyl Mercaptan (CH_3SH)	0.5 / 10	0.5	13.5	10 @ 0.14 ml/min

Two gases (ethylene and methional) used are both toxic and flammable and are therefore listed in both tables. The PDF and XPD beamlines will use boil-off gaseous nitrogen (GN_2) from the NSLS-II utility system. The NSLS-II GN_2 system should provide adequate flow for nearly continuous 10 SCFM flow without the need to change compressed gas cylinders. During experimental operations, minimal down-time is desirable for recurring tasks such as sample change, and experiment set-up; the sample environment therefore uses quick-change fittings and other methods to allow rapid experimental set ups. Additionally, the use of engineering controls (sensor and circuitry) are included to prevent accidental hazardous gas release into occupied spaces.

CONCLUSIONS

The capability to safely use a variety of hazardous gases is needed for in-situ and in-operando X-ray diffraction studies. The chamber and system described herein safely contains hazardous gases while reacting with materials being studied, dilutes the hazardous gases to safe breathing levels, and then exhausts the effluent safely. A hazard analysis was conducted with mitigations for each hazard. Engineering and chemical compatibility studies were also undertaken for each component, gas, and material to assure all requirements were met. The exhaust flow needs for each branch were considered and ducts were all sized for ample flow.

ACKNOWLEDGEMENTS

Several BNL staff members provided review, direction, and guidance. BNL's Safety and Health Services personnel (Michael Gaffney, Mario Cubillo, and Joeseph Terranova) provided ongoing review and guidance, as did the NSLS-II Environmental, Safety and Health staff (Lori Stiegler, and Robert Lee).

The sample environment requires two additional systems for safe operation, an external exhaust system and a fire protection system. Thanks go to BNL's Fire Protection Engineer Michael Kretschmann for design oversight of the fire protection system and to Modernization Plant Office engineer Sriya Adhya for the local connections. Also thanks go to Al Boerner and BNL Electricians for wiring and Chris Stebbins for task coordination.

The GHS referenced herein was designed, built, and installed by Applied Energy Systems (AES) company of Malvern, Pennsylvania, USA with some support and guidance from Mark Winter of Abbie Gregg Incorporated in Tempe, Arizona, USA. Thanks go to AES President Steven Buerkel and Project Manager Robert Holloway who may acknowledge and thank the numerous AES personnel individually. Without the GHS, hazardous gases could not be provided safely.

Lastly, thanks go to Kristen Rubino for the assistance in putting this paper together.