JMEPEG (2004) 13:282-286
DOI: 10.1361/10599490419199

Results of Testing Various Natural Gas Desulfurization Adsorbents

Gordon Israelson

(Submitted 20 November 2003)

This article presents the results of testing many commercially available and some experimental sulfur adsorbents. The desired result of our testing was to find an effective method to reduce the quantity of sulfur in natural gas to less than 100 ppb volume (0.1 ppm volume). An amount of 100 ppb sulfur is the maximum limit permitted for Siemens Westinghouse solid oxide fuel cells (SOFCs). The tested adsorbents include some that rely only on physical adsorption such as activated carbon, some that rely on chemisorption such as heated zinc oxide, and some that may use both processes. The testing was performed on an engineering scale with beds larger than those used for typical laboratory tests. All tests were done at about 3.45 barg (50 psig). The natural gas used for testing was from the local pipeline in Pittsburgh and averaged 6 ppm volume total sulfur. The primary sulfur species were dimethyl sulfide (DMS), isopropyl mercaptan, tertiary butyl mercaptan, and tetrahydrothiophene. Some tests required several months to achieve a sulfur breakthrough of the bed. It was found that DMS always came through a desulfurizer bed first, independent of adsorption process. Since the breakthrough of DMS always exceeds the 100 ppb SOFC sulfur limit before other sulfurs were detected, an index was created to rate the adsorbents in units of ppm DMS × absorbent bed volume. This index is useful for calculating the expected adsorbent bed lifetime before sulfur breakthrough when the inlet natural gas DMS content is known. The adsorbents that are included in these reports were obtained from suppliers in the United States, the Netherlands, Japan, and England. Three activated carbons from different suppliers were found to have identical performance in removing DMS. One of these activated carbons was operated at four different space velocities and again showed the same performance. When using activated carbon as the basis of comparison for other adsorbents, three high-performance adsorbents were found that removed about 100 to 150 times as much DMS as activated carbon before breakthrough.

Keywords adsorbents, desulfurization, natural gas

1. Introduction

In 2000, Siemens Westinghouse (Pittsburgh, PA) started a program to develop a strategic supplier of a natural gas desulfurization process. This began with a testing program to characterize the efficiency of the various adsorbents. The purpose of the natural gas desulfurization-testing program was to gather the information needed to choose a process to be included in the solid oxide fuel cell (SOFC) balance of plant (BOP) systems for desulfurizing natural gas. The process is required to be cost-effective with the following criteria:

- Low initial cost
- Low operational and maintenance costs
- Low or no parasitic power consumption
- Minimal complexity of supporting equipment
- Reliable
- Minimal affect on environment due to regeneration or disposal.

2. Background

Early Siemens Westinghouse testing of SOFCs produced a sulfur acceptance limit of 0.1 ppm volume (ppmv). This limit had been judged to be the sulfur (S) level at which the SOFC voltage drop was sufficient to cause an undesirable performance degradation. In year 2000, some additional testing was done to quantify the performance degradation.[1] These tests exposed SOFCs to different levels of hydrogen sulfide, H_2S. These exposure levels were 0.3, 1, and 3 ppmv. Figures 1, 2, and 3 show voltages of two different SOFCs that were manufactured using differing processes and that had differing performance under the same operating conditions.

The point to be made from these test results is that a well-defined drop in cell voltage occurred shortly after exposure to hydrogen sulfide. The amount of the voltage reduction was greatest for the highest concentration of sulfur but was still very significant for a low level (0.3 ppmv). Upon removal of H_2S, the cell performance recovered. The higher the concentration of H_2S, the longer it takes for SOFC performance recovery.

This paper was presented at the Fuel Cells: Materials, Processing, and Manufacturing Technologies Symposium sponsored by the Energy/Utilities Industrial Sector & Ground Transportation Industrial Sector and the Specialty Materials Critical Technologies Sector at the ASM International Materials Solutions Conference, October 13-15, 2003, in Pittsburgh, PA. The symposium was organized by P. Singh, Pacific Northwest National Laboratory, S.C. Deevi, Philip Morris USA, T. Armstrong, Oak Ridge National Laboratory, and T. Dubois, U.S. Army CECOM.

Gordon Israelson, Stationary Fuel Cells, Siemens Westinghouse Power Corporation, 1310 Beulah Road, Pittsburgh, PA 15235. Contact e-mail: gordon.israelson@siemens.com.

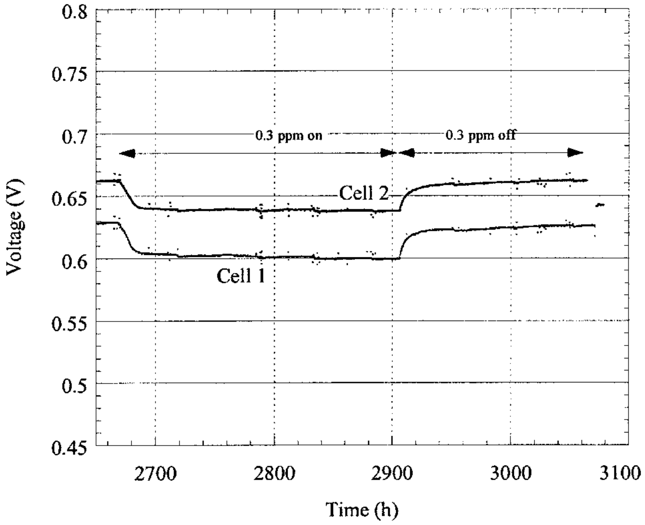

Fig. 1 SOFC voltage reduction and recovery from exposure to 0.3 ppmv H_2S

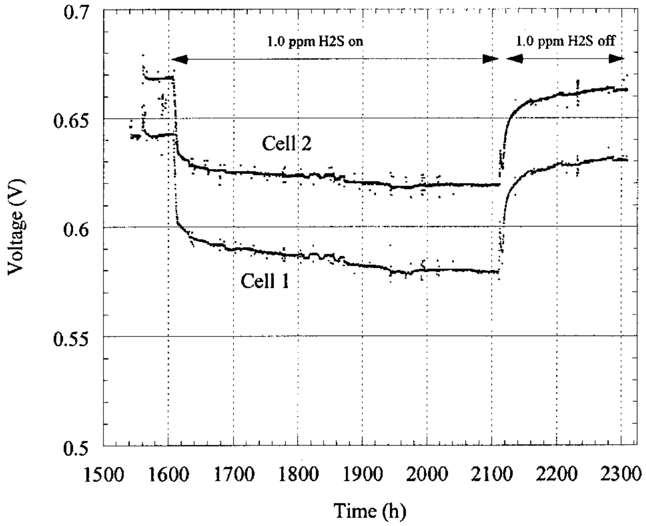

Fig. 2 SOFC voltage reduction and recovery from exposure to 1 ppmv H_2S

3. Desulfurization Testing

3.1 Test Setup

Most testing was performed using test vessels designed by Siemens Westinghouse. These were designed for general use with any desulfurization adsorbent. The Siemens Westinghouse desulfurization test vessel is an assembly of 5.08 cm (2 inches) stainless steel pipe with flanged ends. It is mounted vertically. It has sample taps located at 5.08 cm (2 inch) intervals along its entire length. The taps are suitable for placing a sample probe into the bed or inserting a 3.18 mm (1/8 inch) thermocouple probe. The sample probes are 3.18 mm (1/8 inch) tubes, welded shut at one end and having four tiny 0.40 mm (1/64 inch) holes drilled into the underside of the tube. The holes are equally spaced across the 5.08 cm (2 inch) inside width of the vessel. This allows the drawing of a combined sample to represent the gas composition at the plane of the probe. Within a vessel, the adsorbent is supported by a fine screen that is in turn supported by a coarse screen. Siemens Westinghouse testing is done with four vessels that can be operated independently and simultaneously. Flow through the vessels can be aligned to pass in series or in parallel.

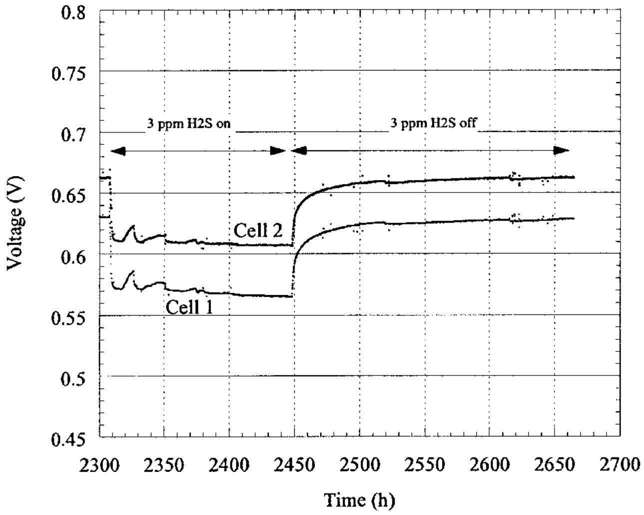

Fig. 3 SOFC voltage reduction and recovery from exposure to 3 ppmv H_2S

The test facility includes equipment that can add hydrogen (H_2) or heat or both to a vessel that contains a desulfurization adsorbent. The system can control any natural gas pressure from atmospheric pressure to the pressure limit of the vessel design of 10.35 bar guage (barg) [150 psi guage (psig)]. For example, two vessels can be used in series to test a heated cobalt molybdenum bed upstream of a heated zinc oxide bed, while the other two vessels can operate independently at ambient temperature.

Natural gas is introduced into the vessel at its upper end and is removed from the lower end. Prior to entering the top of the vessel, the gas passes through tubing that runs along the outside of the vessel from the bottom to the top. This tubing is inside of the vessel heaters. In this manner, the natural gas is preheated before it enters the top of the test vessel. The vessel interior, the bed support screens, the sample probes, and the sample tubing are passivated with the Silcosteel (Restek Corp., State College, PA)[1] process to prevent inadvertent contamination by residues of previous samples. The vessel is designed and built per ASME B&PV code requirements for 20.70 barg (300 psig) and 400 °C (750 °F) design conditions, even though it will normally operate at about 3.45 barg (50 psig) at temperatures ranging from ambient to 370 °C (700 °F). This high design pressure was selected to accommodate a potential internal deflagration of natural gas.

Three suppliers of adsorbents provided samples for testing within their own vessels. These vessels were sealed, having only a gas inlet port and gas outlet ports. Little detail of the internal arrangements was provided to Siemens Westinghouse. These sealed adsorbent vessels were provided by supplier C, supplier E, and Pacific Northwest National Laboratory (PNNL) (Richland, WA). Subsequent to the Siemens Westinghouse testing of its material, PNNL has released for public knowledge the composition of their material. This public disclosure was at the Fuel Cell Seminar in Palm Springs, CA, in November 2002.[2]

Most testing was performed at ambient temperature (about 21 °C [70 °F]) and 3.45 barg (50 psig) to simulate the conditions expected in a commercially viable desulfurizer. Two materials were tested at the same pressure, but at elevated temperatures. The adsorbents were obtained from domestic US suppliers and foreign suppliers in The Netherlands, Japan, and England.

This test was arranged to be an engineering test that would process relatively large quantities of natural gas. It was necessary to use the S concentrations provided with the site pipeline natural gas. The types and amounts of S compounds in the pipeline gas were not known at the start of the test. Accordingly, the inlet gas S analysis was made often during the testing. Because the concentration of S compounds in the inlet gas varied, it was not possible to test the adsorbents with the same inlet S concentrations.

The method selected for measuring the natural gas S content before and after processing is S-specific chemiluminescence (SCD). An SCD detector on a gas chromatograph produces distinctive response peaks that are linearly proportional to the quantity of S in each compound. The significant advantage of SCD over the other technologies is its ability to discriminate between the different S compounds. Not only can the total amount of S be measured, but S levels can be determined by chemical type. In our testing, a concentration of about 20-30 ppb volume (ppbv) or greater of any S species could be resolved.

The SCD gas chromatograph was regularly calibrated using a heated permeation tube-based gas standards generator. Hydrogen sulfide, dimethyl sulfide (DMS), tetrahydrothiophene, and tertiary butyl mercaptan permeation tubes were used to produce known gas standards of 500 ppbv to 5 ppmv concentration.

3.2 Test Results: General Observations

The testing of various materials for their capability to adsorb the S-bearing contaminants in natural gas provided several surprises. These surprises and other observations are as follows:

1) A literature review and discussions with adsorbent suppliers gave the popular wisdom that tetrahydrothiophene would be the most difficult contaminant to remove. The test results showed that DMS was the least adsorbed material followed by tertiary butyl mercoptan (TBM). All adsorbents, both physical adsorption and chemisorption types, passed DMS first. Because the breakthrough of DMS always exceeded the 100 ppbv limit for SOFCs before a different S species broke through, the desulfurizer design that removes DMS for a sufficient time will also remove all other S compounds.
2) All activated carbons, including the ones impregnated with various metal oxides to promote S removal, have a low capacity to remove DMS. They also have little capacity for removing TBM. When the number of bed volumes of natural gas that were desulfurized is multiplied by the average DMS content of the inlet gas, the resulting number is very similar for the three activated carbons. This value for activated carbons is about 25,000 ppmv DMS × bed volume.
3) A test of zinc oxide was performed to see if it would catalyze and remove S compounds when operated at 343-371 °C (650-700 °F) without excess H_2 being added to the inlet natural gas feed stream. Testing without excess H_2 showed practically no DMS adsorption capacity for zinc oxide. Testing with excess H_2 has not been performed and is not scheduled because a means to supply H_2 for fuel desulfurization produces an undesirable BOP complexity for SOFCs.

Table 1 Natural Gas Composition during Desulfurization Adsorbent Testing

Component	Vol. % (20 Feb. 2002 Sample)	Vol. % (30 Jan. 2001 Sample)
Methane	95.43	89.03
Ethane	3.08	3.15
Propane	0.54	2.17
Iso-butane	0.010	1.09
Butane	0.13	1.03
Iso-pentane	0.05	0.39
Pentane	0.04	0.38
Hexane	<0.01	0.53
Nitrogen	0.63	2.22
Carbon dioxide	<0.01	<0.01
Specific gravity	0.5817	0.6576
BTU value		
Dry	1045	1137
Saturated	1027	1117

Since there was no regular analysis of natural gas hydrocarbon composition, there is no information about any possible effects of the presence of higher hydrocarbons interfering with the adsorption of S compounds. Table 1 shows the analysis of two samples of the site pipeline natural gas during the period of testing. The pipeline natural gas water vapor content is also unknown. Our goal was to find an effective desulfurization process that works with natural gas as it comes out of the pipeline. Artificially drying the natural gas before passing it through the desulfurization process would provide results of little value for the purposes of this research project.

The testing was performed at natural gas pressures that are typical of those expected during commercial fuel cell plant desulfurization (~3.45 barg [50 psig]). There was no attempt to characterize any changes in the adsorption of S with varying pressure.

Because of the wide variation of total S and relative quantities of the types of S in the inlet natural gas, there was no correlation between the total S removed and the breakthrough of DMS. The best index to predict the breakthrough of DMS is as follows: average ppmv DMS × cubic feet of natural gas/cubic feet of adsorbent.

When an adsorbent is removing a S species, it is removing it all or at most to the limit of resolution of the S analyzer, or about 20-30 ppbv. When the species breaks through, the ap-

Table 2 Desulfurization Adsorbent Testing Results

Manufacturer	Active Component	Product Name	Ave. DMS, ppmv	Ave. Total Sulfur, ppmv	Performance Index, ppmv DMS Bed Volumes
United Catalysts, Inc. (Süd-Chemie)	ZnO at 350 °C (no preceding CoMo catalyst bed or hydrogen addition)	G-72E	1.5	6.7	668
Norit	Carbon with chromium and copper salts	RGM-3	0.8	5.1	24 000
Calgon Carbon	Carbon	PCB	1.5	6.2	26 550
Süd-Chemie	Carbon with copper oxide	C8-7-01	1.8	6.7	27 900
Süd-Chemie	Nickel, nickel oxide (unheated)	C28	1.1	4.2	44 992
Grace Davison	Molecular sieve; 13× (10 Å pore) zeolite-X	554HP	0.8	4.4	110 376
Supplier C	Unknown	Proprietary adsorbent S	1.2	5.1	182 573
PNNL	Copper-impregnated zeolite-Y substrate	Unnamed	0.8	4.1	2 416 800
Synetix	Copper oxide and zinc oxide, 100 °C top, 170 °C bottom	Puraspec 2084	3.4	8.4	3 661 800
Supplier E	Unknown	Proprietary adsorbent T	2.3	8.2	3 813 400

pearance of S on a chromatogram is usually well defined, and the concentration increases rapidly with time, as seen on successive chromatograms. Our testing could produce a new chromatogram every 20 min. The adsorptions of the various species seem to be independent of each other, with the breakthrough always occurring in the same order.

3.3 Test Results: Details

The testing process was performed to identify the most cost-effective method to reduce the S content of natural gas fuel to less than 0.1 ppmv (100 ppbv). Because of confidentiality agreements with suppliers of the desulfurization adsorbents, no pricing or cost-effectiveness analysis can be provided here. The DMS desulfurization capacity results alone are provided.

Some of the adsorbents were tested under conditions outside of the manufacturer's recommendations. This was to investigate whether the absorbent may be useful for the Siemens Westinghouse SOFCs. Where this was the situation, the discussion will note that fact. The results of the desulfurization testing are summarized in Table 2.

None of the suppliers of zinc oxide ever made any claim that zinc oxide will catalyze and adsorb S compounds from natural gas when excess H is not available. The Süd-Chemie (Süd-Chemie, Inc., Louisville, KY) ZnO was operated at 175 °C (350 °F) and also at 370 °C (700 °F) at a space velocity (i.e., the volume of natural gas at standard conditions that passes through the adsorbent bed) of 156 bed volumes/h. These tests were easy to perform and showed that zinc oxide, at moderate (175 °C) and normal (370 °C) operating temperatures, has effectively no capacity to adsorb DMS when there is no excess H.

The Norit (Norit Americas, Inc., Atlanta, GA) activated carbon was tested at four space velocities; 254, 508, 762, and 1016 bed volumes/h. The Calgon (Calgon Carbon Corporation, Pittsburgh, PA) and Süd-Chemie carbons (C) were tested at space velocities of 158 and 157 bed volumes/h, respectively. All carbons at all space velocities showed that same capacity for DMS, about 25,000 ppmv DMS × bed volume.

The Süd-Chemie product C28 is intended by its manufacturer to be heated to 175 °C (350 °F). Because it is desired that the BOP not require the additional complexity of adding heat to the desulfurization adsorbent, it was tested unheated. C28 performance was slightly less than twice as good as activated C for DMS removal. The space velocity was 333 bed volumes/h.

The Grace-Davison (W.R. Grace and Company, Columbia, MD) zeolite-X molecular sieve removed 4.4 times as much DMS as the same volume of activated C before breakthrough. The space velocity was 360 bed volumes/h.

The Supplier C proprietary adsorbent S material was provided within its own sealed vessel. It was operated at a space velocity of 328 bed volumes/h and removed more than seven times as much DMS as an equal volume of C.

PNNL developed a copper-impregnated zeolite-Y desulfurization adsorbent. It was supplied in its own sealed vessel. When operated at a space velocity of 1621 bed volumes/h, it removed about 100 times as much DMS as carbon.

The Puraspec 2084 adsorbent by Synetix (Johnson Matthey Catalysts, Billingham, UK) is intended to operate above ~150 °C (300 °F) and ideally at ~200 °C (400 °F). Our test rig had a temperature control problem, and the bed was operated at 100 °C (210 °F) at its top and 170 ° (340 °F) at its bottom. Even though it was not uniformly heated to its optimum temperature, it still removed almost 150 times as much DMS as C. It was operated at a space velocity of 446 bed volumes/h. Puraspec 2084 relies upon catalysis and chemisorption of the S compounds. The resulting metal sulfides are pyrophoric and must be handled accordingly when unloading.

The best performer of the desulfurization adsorbents was proprietary adsorbent T supplied by supplier E. The sample was provided in its own sealed test vessel. When operated at a space velocity of 1207 bed volumes/h, it removed more than 150 times as much DMS as activated C. The adsorption process is physical adsorption. The material was tested for pyrophoric behavior, and no heating was detected when air passed through the vessel.

4. Conclusions

Testing showed DMS to be the most difficult S compound to remove from pipeline natural gas at 3.45 barg (50 psig). It always came through an absorbent bed before any other S compound. This was true for both physical adsorption and chemisorption processes. Its concentration after breakthrough always exceeded our 100 ppbv limit for SOFCs before the next S species, IPM, came through. IPM was always the next S species to break through.

Three activated C supplied by different manufacturers all showed the same capacity for DMS removal before they were exhausted. Four beds of one of these operated at four different space velocities all showed the same capacity for DMS removal before they were exhausted. This value was 25,000 ppm DMS × bed volume. There are several commercially available desulfurization adsorbents that surpass activated carbon for the capacity to remove DMS.

Two developmental adsorbents that rely on physical adsorption, and one heated chemisorption adsorbent, had two orders of magnitude greater capacity to remove DMS than an equal volume of activated C.

Acknowledgment

The desulfurization adsorbent testing work was partially funded by the US Department of Energy. The work was performed under Task 5.2.6 of Department of Energy contract DE-FC26-97FT 34139.

References

1. G. Tomlins: Unpublished research report, Siemens Westinghouse Power Corp., Stationary Fuel Cells Division, Pittsburgh, PA.
2. D.L. King, J.C. Birnbaum, and P. Singh: "Sulfur Removal From Pipe Line Natural Gas Fuel: Application To Fuel Cell Power Generation Systems," *Pacific Northwest National Laboratory* (*PNNL*), *Fuel Cell Seminar,* Palm Springs, CA, November 18-21, 2002.