

## **PEROVSKITE SORBENTS FOR REMOVAL OF SULFUR, ARSENIC AND PHOSPHORUS**

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Solid sorbents are being developed to reduce concentrations of sulfur, arsenic and phosphorus in synthesis gas and water-gas shift mixtures from parts-per-million by volume (ppmv) concentrations to no more than 1–2 parts-per-billion by volume (ppbv) in the presence of steam. To prevent poisoning of nickel catalysts used in solid oxide fuel cells (SOFC), sulfur concentrations must be reduced to below 60 ppbv [1]. Arsenic and phosphorus concentrations must also be reduced to below 5 and 1–2 ppbv, respectively. The platinum catalysts of proton exchange membrane (PEM) fuel cells are even more susceptible to poisoning, unable to withstand over 4 ppbv of sulfur [1]. PEM fuel cells will require hydrogen of the highest purity—likely requiring hydrogen purification membranes—which in turn require protection from sulfur, arsenic and phosphorus. Commercial palladium-silver based membranes for hydrogen purification will not tolerate more than 4 ppbv H<sub>2</sub>S, depending upon operating conditions, due to formation of a bulk Pd<sub>4</sub>S. The sorbents under development bind sulfur more tightly than any other materials, thus greatly reducing the pressures of H<sub>2</sub>S and COS relative to conventional sorbents based upon zinc or iron. These polishing sorbents are designed to operate at 300°C, which complements bulk sulfur sorption, water-gas shift and palladium membrane technologies. In addition, these sorbents form phosphates and arsenates with high thermal stabilities, thereby reducing the concentrations of arsenic and phosphorus species, including As<sub>4</sub>, AsH<sub>3</sub>, P<sub>4</sub>, PH<sub>3</sub>, HPO<sub>2</sub> and HPO<sub>3</sub>. Calculations indicate that strongly binding sulfur will reduce the equilibrium partial pressure of H<sub>2</sub>S even in the presence of high-pressure steam to immeasurably low concentrations ( $\leq 1$  pptv). Thermogravimetric analysis (TGA) shows that preferred sorbents capture over 7 wt% sulfur at 300°C. In addition, TGA has been used to study regeneration by temperature-swing desorption at 500°C and above—showing over 15 wt% cumulative sulfur capture and regenerability through 20 cycles. Breakthrough tests under simulated sulfur-contaminated water-gas shift conditions (40% steam by volume) indicate total sulfur levels well below the current limits of detection (< 70 ppbv). Control experiments using commercial Cu/ZnO sorbents under identical breakthrough conditions show total sulfur concentrations at or above 117 ppbv throughout the breakthrough test—indicating that the Eltron sorbents are superior to zinc-based sorbents under steam. In addition to high sulfur capacity, Eltron sorbents show arsenic and phosphorus capture of nearly 5 wt% during 3-hour exposure tests.

### **Coal Derived Hydrogen for Electricity and Chemicals**

The United States consumes 1 billion metric tons of coal annually [2]. Of this, approximately 900 million metric tons is utilized for generation of electric power [2]. Integrated Gasification Combined Cycle (IGCC) electric power plants utilizing hydrogen turbines or SOFCs have the potential for improving overall efficiency from about 33% (achieved by conventional fossil fuel and nuclear electric power plants) to 45–50% [3]. Improved efficiency across the entire fleet of coal-burning power plants could save up to 300 million tons of coal annually while simultaneously cutting CO<sub>2</sub> production at U.S. power plants by one third. In addition, new IGCC power plants have the potential to essentially eliminate all CO<sub>2</sub> emissions. Use of dense hydrogen transport membranes to separate hydrogen from CO<sub>2</sub> downstream of water-gas shift reactors would provide non-polluting hydrogen to turbines and fuel cells while

retaining CO<sub>2</sub> at the high concentration and pressure necessary to further reduce the costs associated with CO<sub>2</sub> sequestration (i.e., compression and pipeline transportation) [4].

However, impurities originating from coal will need to be reduced to extremely low levels to avoid damaging high-speed, hydrogen-powered turbines or avoid poisoning the nickel catalysts used in the anodes of SOFCs [5,6] envisioned by the U.S. Department of Energy (DOE) for Integrated Gasification Combined Cycle Fuel Cell (IGCCFC) power plants. SOFCs will be permanently damaged if bulk nickel sulfides form and melt (m.p. NiS = 797°C and Ni<sub>3</sub>S<sub>2</sub> = 790°C), destroying the physical and mechanical integrity of the anodes. Table 1 lists some stated target concentrations of select impurities as recommended by the DOE [1]. Note that to protect nickel catalysts in SOFCs for IGCCFC power plants, total sulfur will need to be lowered to 60 ppbv and arsenic to 5 ppbv.

**Table 1.** DOE Polishing Filter Technical Targets [1]

Contaminant	Gas Turbine	SOFC	PEM Fuel Cells
Total Sulfur (H <sub>2</sub> S, COS, CS <sub>2</sub> , etc.)	20 ppmv	60 ppbv	4 ppbv
Metals	20 ppbw Pb 10 ppbw V 40 ppbw Ca 40 ppbw Mg	5 ppbv As 200 ppbv Se 30 ppbv Cd	Not specified
Total Halides (Cl, F, Br)	5 ppmv	100 ppbv	50 ppbv
Total Alkalis (Na, K, Li)	100 ppbv	Not specified	Not specified

The goal of this research is to design and develop solid sorbents for use in polishing systems operating under warm-gas cleaning conditions (250°C–350°C) in steam and coal-derived water-gas shift mixtures. This polishing sorbent system must reduce concentrations of sulfur and its compounds from 1–20 ppmv, now achieved by existing sorbents, to very low ppbv (1–2 ppbv) levels. Dense palladium-catalyzed hydrogen transport membranes are envisioned for ultimate gas clean-up, eliminating essentially all impurities and purifying hydrogen to the highest possible levels while retaining CO<sub>2</sub> at very high concentration and pressure, up to 1000 psi (69 bar) for economic sequestration. However, for palladium-based membranes to function, impurities (especially sulfur, arsenic and phosphorus) that poison palladium, must be reduced, preferably to ppbv concentrations. Especially damaging to membranes is the formation of bulk Pd<sub>4</sub>S.

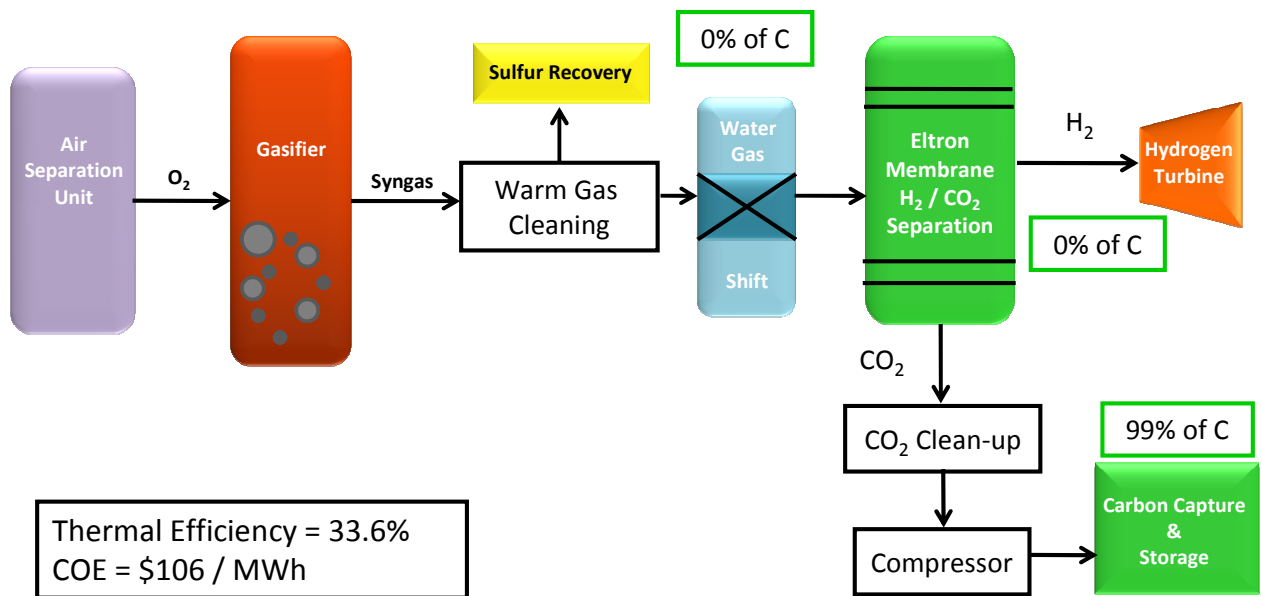
### Benefits of Warm Gas Cleanup with Hydrogen Transport Membrane

The economic benefits of using warm gas cleanup combined with Eltron's hydrogen transport membrane system for CO<sub>2</sub> capture in IGCC plants were outlined in a techno-economic analysis [7]. Three separate cases are shown in Table 2. The base case (Case 1) uses conventional cold gas (Selexol) technology for sulfur removal and CO<sub>2</sub> separation downstream of a high pressure General Electric (GE) gasifier, quench cooling and water-gas shift. Case 2 uses the GE gasifier, followed by conventional cold gas amine (MDEA) treating for sulfur removal, water-gas shift, and Eltron's membrane system for H<sub>2</sub>/CO<sub>2</sub> separation. Radiant-convective cooling of syngas from the gasifier is used in Case 2 to avoid high moisture content in the feed to the amine absorber before the shift reactors. Thermal efficiency is improved in this case (partly due to the gasifier cooling method), while cost of electricity decreases slightly. A similar configuration is used in Case 3 (see Figure 1) as in Case 2,

substituting warm gas cleaning for the desulfurization step. The cost of electricity in Case 3 decreases by \$9.50 per MWh over the base case, with a 6% increase in thermal efficiency (see Table 2). Another benefit of the combination of warm gas cleaning and the hydrogen membrane is a significant increase in CO<sub>2</sub> capture from 90% to 99%.

**Table 2.** Summary of Economic Results for the Techno-Economic Analysis of CO<sub>2</sub> Capture in IGCC Plants

Pre-combustion Gas Cleaning & CO <sub>2</sub> Capture Method	Case 1: 2-Stage Selexol	Case 2: Cold Gas Cleaning & Eltron Membrane	Case 3: Warm Gas Cleaning & Eltron Membrane	Improvement of Case 3 over Base Case
Thermal Efficiency	27.4%	32.0%	33.4%	6.0%
% CO <sub>2</sub> Captured	90%	90%	99%	9%
Cost of Electricity (\$/MWh)	115.5	114.5	106.0	9.5



**Figure 1.** Case 3: CO<sub>2</sub> Capture with Warm Gas Cleaning and Eltron's H<sub>2</sub> Separation Membrane.

### Drawbacks of the Zn-Based Sulfur Sorbent Systems

According to DOE guidelines [8], a baseline 640 MW<sub>e</sub> IGCC electric power plant will consume 225 metric tons of Illinois #6 coal per hour and will produce 509 metric tons of CO<sub>2</sub> per hour. Using the recommended sulfur content (2.5 wt%) of Illinois #6 bituminous coal [8], a desulfurization system must remove 5.6 metric tons of sulfur per hour.

The sulfur polishing filters under development in the present research are intended to be placed downstream of a first-stage IGCC sulfur-removal system such as that now under development by Research Triangle Institute (RTI) and Eastman [9,10]. The RTI/Eastman system uses Zn-based sorbents to reduce sulfur concentration by 99.90% [10]. Therefore, 0.10% of the input sulfur ( $\approx 6$  kg/hr) will exit the RTI system—resulting in sulfur gases of sufficient concentration for the formation of sulfides that will rapidly destroy either fuel cells or hydrogen transport membranes. RTI reports H<sub>2</sub>S levels exiting their system at 3–20 ppmv [10].

Zn-based sorbents such as Cu/ZnO are theoretically capable of bringing concentrations of sulfur to pptv concentrations under dry conditions. However, under high-pressure steam, H<sub>2</sub>S is released by the equilibrium reaction: ZnS + H<sub>2</sub>O = ZnO + H<sub>2</sub>S [5]. Breakthrough experiments conducted at Eltron Research & Development using commercial Cu/ZnO sorbents under water-gas shift conditions (40% steam by volume) show total sulfur concentrations in excess of 117 ppbv.

## Sulfur Sorbent Screening

In order to rapidly screen new sorbent compositions, materials are exposed to sulfur as H<sub>2</sub>S during TGA analysis. Using TGA, sorbent candidates are pre-reduced at 300°C in 10% H<sub>2</sub> (balance Ar) for 3 hours in order to remove a small percent of the lattice oxygen. Pre-reduction is followed by sulfur exposure at 300°C in 155 ppmv H<sub>2</sub>S (balance Ar) for 10 hours. Since these tests are time-limited, none of these numbers reflect the full sulfur capacity of these sorbents. In these tests, a sorbent sample is placed into an 85 µL Al<sub>2</sub>O<sub>3</sub> TGA crucible, open on top. The crucible is then placed into a Netzsch STA 449 F3 Simultaneous Thermal Analyzer for TGA tests. To date, 66 different screening tests have been performed on nearly 40 distinct materials. Long-term TGA testing has also been performed to determine the saturated sulfur capacity of sorbents. Eltron sorbents have been shown to capture over 7 wt% sulfur at 300°C.

Table 3 summarizes mass gain in terms of milligrams of sulfur sorbed per gram of sorbent (mgS·g<sup>-1</sup>) for select materials after 10 hours at 300°C in 155 ppmv H<sub>2</sub>S (balance Ar). Values of sulfur uptake for some of the newly developed sorbents meet or exceed that of commercial Cu/ZnO. It should also be noted that values of mass gain listed in Table 3 exceed that which can be explained by surface adsorption—suggesting the formation of bulk sulfides which has also been verified by x-ray diffraction.

**Table 3.** Comparison of Unsaturated Sulfur Capacity at 300°C Before and After Attrition Milling.

Sorbent	Before Attrition Milling		After Attrition Milling	
	Surface Area (m <sup>2</sup> ·g <sup>-1</sup> )	Unsaturated Capacity (mg S·g <sup>-1</sup> sorbent)	Surface Area (m <sup>2</sup> ·g <sup>-1</sup> )	Unsaturated Capacity (mg S·g <sup>-1</sup> sorbent)
K53	0.3	15–18	10.1	28–29
K56	0.1	16	5.1	27
K57	0.1	23–38	6.2	45
K59	0.1	14–22	6.3	33
K60	0.2	16	7.9	30
K61	0.1	22–23	18.1	62
<b>Commercial Sorbents</b>			<b>As Received</b>	
Cu/ZnO	NA	NA	52.6	29
ZnO	NA	NA	40.3	30

Many of the Eltron sorbents have been prepared using solid state synthesis which results in low surface area prior to attrition milling (0.1–0.5 m<sup>2</sup>·g<sup>-1</sup>). Despite the low surface areas, sulfur sorption was considerable for many of the sorbents. Eltron sorbents were attrition milled to reduce particle size and increase surface area (5–20 m<sup>2</sup>·g<sup>-1</sup>). A corresponding increase in sulfur capacity was also observed (see Table 3). Sorbents of the same composition

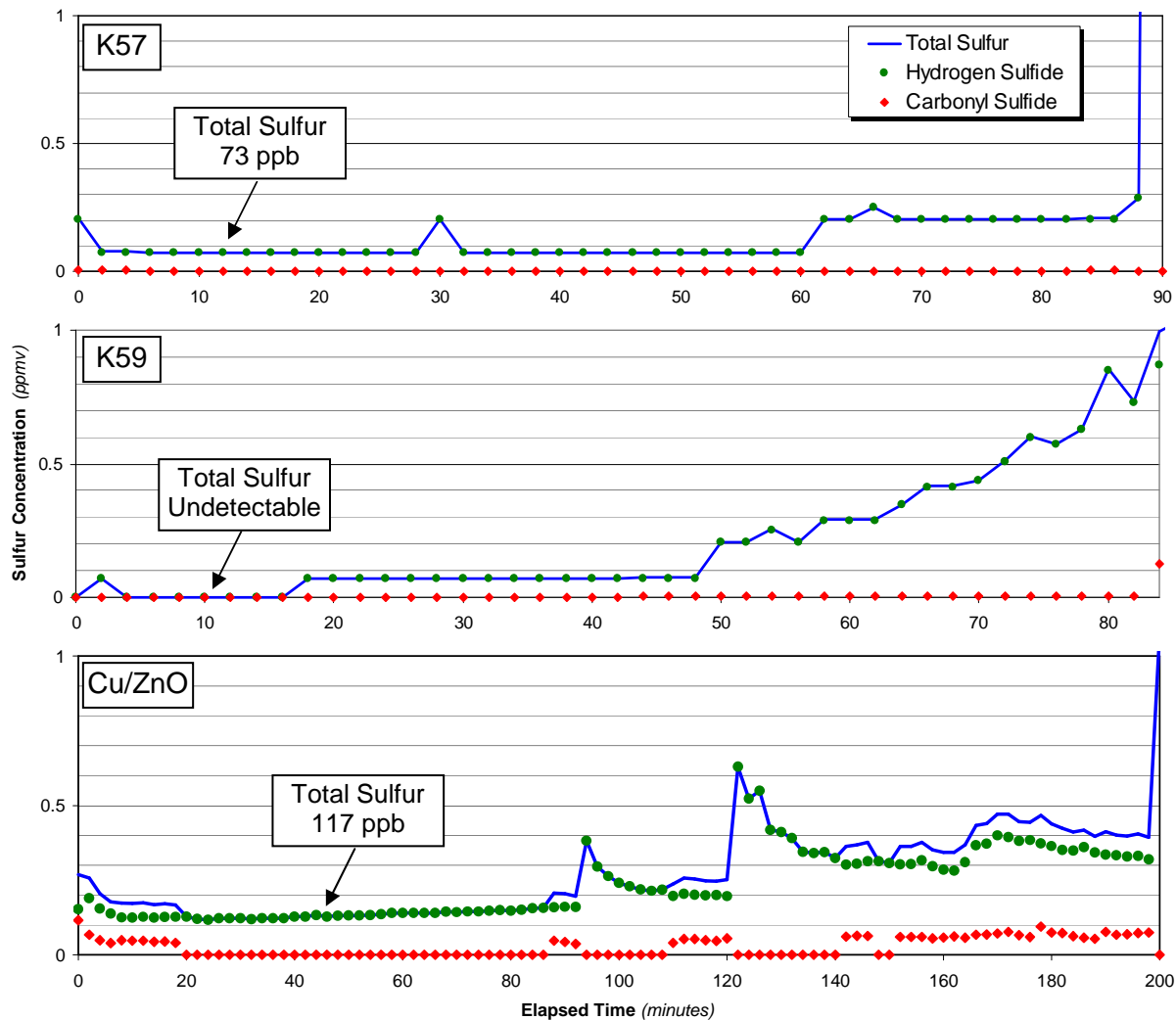
were also prepared using nitrate precipitation to yield high surface areas ( $> 50 \text{ m}^2\cdot\text{g}^{-1}$ ). Further increases in sulfur sorption capacity were not observed, and these high surface area sorbents were shown to lose surface area upon exposure to high regeneration temperatures.

## H<sub>2</sub>S/COS Breakthrough Testing

Sulfur breakthrough tests were performed by exposing a packed bed of sulfur sorbent material to a simulated water-gas shift stream at 300°C containing by volume 40% H<sub>2</sub>O (steam), 18% CO<sub>2</sub>, 40% H<sub>2</sub>, 3% CO, and 155 ppmv H<sub>2</sub>S. Breakthrough was defined to be the point when total sulfur slippage first exceeded 1 ppmv. Gas delivery was from custom mixed tanks using mass flow controllers (MFCs). Water was admitted to the system via a liquid MFC and raised to make steam. The steam and the simulated water-gas shift streams were then combined and delivered to the sorbent test bed. In order to maximize the sulfur uptake prior to breakthrough, the sorbents were pre-reduced at 300°C under flowing H<sub>2</sub> at 300 sccm (STP at 0°C and 10<sup>5</sup> Pa) for 3 hours prior to sulfur exposure. By utilizing a small (5 mL) packed sorbent bed, a space velocity of 6000 hr<sup>-1</sup> was achieved during sulfur exposure from a total gas delivery rate of 500 sccm. A high aspect ratio (length to cross-sectional area) bed geometry was used to minimize deleterious effects related to reaction kinetics.

The H<sub>2</sub>S, COS and SO<sub>x</sub> concentration were monitored throughout the breakthrough tests by continuous, automated GC sampling (500 μL Sulfinert<sup>®</sup> sample loop; Sulfinert<sup>®</sup> treated VICI injection valve). A Shimadzu GC-14A equipped with an FPD-14B detector and a Supelco (Bellefonte, PA) Model 12255-U packed GC column were employed to analyze the post-sorbent gas stream. The GC column was operated isothermally at 50°C (He carrier gas; 60 kPa)—resulting in a 2 minute chromatogram with adequate separation of H<sub>2</sub>S, COS, and SO<sub>x</sub> (not observed) within 2 minutes. A multi-point GC calibration was obtained via dilution of calibration standards for H<sub>2</sub>S (1.1 ppmv and 0.42 ppmv) and COS (10.2 ppmv). All standards were mixed and diluted with UHP-grade Ar as the balance gas and supplied from Matheson Tri-Gas. Like the post-sorbent gas streams, the entire calibration assembly is Sulfinert<sup>®</sup> treated stainless steel to minimize sulfur losses throughout the system. Multiple injections were obtained at each calibration level in order to verify that a stable signal was obtained. This chromatography approach is not capable of handling super-saturated steam; therefore, a Nafion<sup>®</sup> gas dryer (Perma Pure, LLC) with counter-flowing nitrogen was utilized to reduce the moisture content of the effluent gas stream to a non-condensing level. Because H<sub>2</sub>S and COS are water soluble gases, great care must be taken to avoid condensing H<sub>2</sub>O at any point in the analysis stream. Based on this technique, quantitative GC analysis was possible for H<sub>2</sub>S concentrations  $\geq 74$  ppbv and COS concentrations  $\geq 10$  ppbv.

Preliminary breakthrough testing indicated that in addition to the release of H<sub>2</sub>S by reaction of steam with ZnS, commercial sorbents of Cu/ZnO release carbonyl sulfide (COS) under water-gas shift conditions. Additional equilibria exist for reactions of CO and CO<sub>2</sub> with ZnS that set the lower limits of COS concentration. Figure 2 shows breakthrough data collected downstream from a commercial Cu/ZnO sorbent exposed to H<sub>2</sub>S contaminated water-gas shift mixtures at 300°C and ambient pressure. At no time were the total sulfur or H<sub>2</sub>S concentrations below 117 ppbv.



**Figure 2.** Breakthrough results for Eltron's K57 (top) and K59 (middle) sulfur sorbents and a commercial Cu/ZnO (bottom) sulfur sorbent. Eltron's sorbents show total sulfur at or below detection limits for nearly an hour. When testing the Cu/ZnO, at no time was the H<sub>2</sub>S concentration below 100 ppb. Feed: 40% H<sub>2</sub>O (steam), 18% CO<sub>2</sub>, 40% H<sub>2</sub>, 3% CO, and 155 ppmv H<sub>2</sub>S at 300°C.

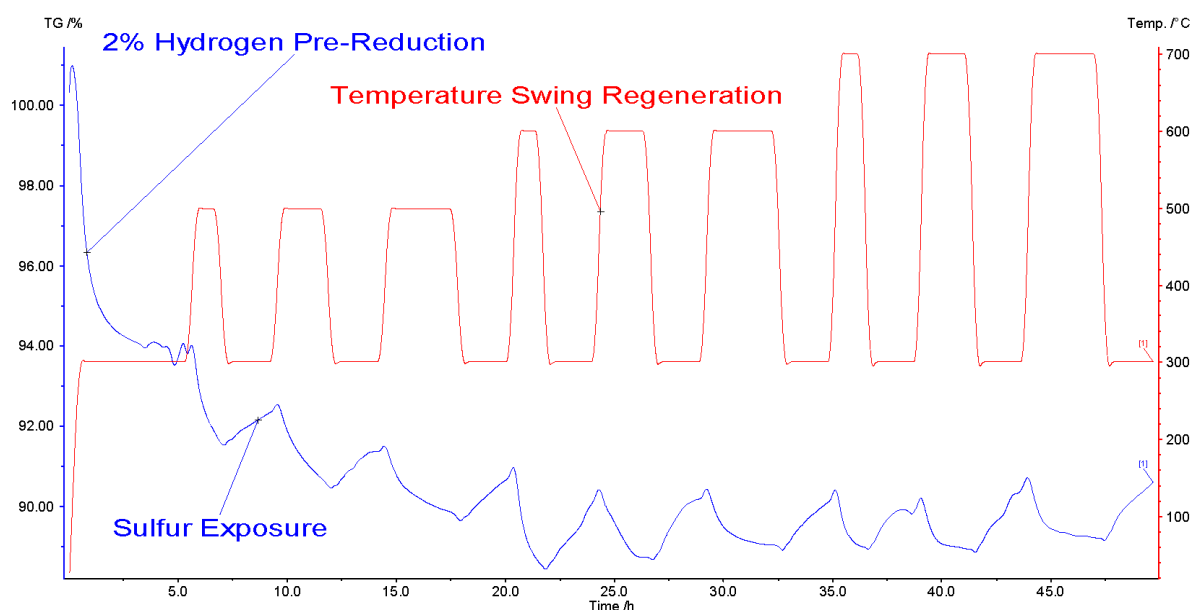
Several of Eltron's sulfur sorbents have been tested in the breakthrough reactor under the procedures described above. Two different Eltron sorbents (K57 and K59) have demonstrated sulfur removal capacities that exceed commercial Cu/ZnO (see Figure 2). Both sorbents show total sulfur at or below detection limits for nearly an hour. Unlike the Cu/ZnO, COS is not observed until the sorbents approach saturation.

### Sulfur Sorbent Regeneration

Cyclic, high-temperature regeneration tests were performed on the Eltron sorbents in order to determine their potential for regeneration in hydrogen. Initial tests assessed the impact of regenerating the sorbents at various temperatures using a mixture of 2% H<sub>2</sub> in Ar in the TGA. The test began by pre-reducing the sorbents in 2% H<sub>2</sub> (balance Ar) for three hours at 300°C. Next the sorbents were cycled between H<sub>2</sub>S exposure (155 ppmv, balance argon) at

300°C for 2 hours and various regeneration segments. As shown in Figure 3, the optimal regeneration step was determined by varying the dwell time (1–3 hr) and temperature (500–700°C) of the regeneration segment. At regeneration temperatures  $\geq 600^\circ\text{C}$ , the sorbent mass gain and loss was nearly the same for each segment. Regeneration is fairly rapid with the majority of the sulfur being liberated from the sorbent during the initial temperature ramp.

20-cycle tests incorporating 2-hour, 500°C regeneration segments were also performed with both the K57 and K59 sorbents. K57 showed 15.3 wt% net sulfur sorption at 300°C after 20 cycles with a 500°C regeneration segment, and K59 showed a net sulfur sorption of 11.1 wt%. In both cases, the 20-cycle tests indicated incomplete regeneration and a subsequent drop in sulfur sorption through the tests. By switching to a 1-hour, 600°C regeneration step, it is anticipated that the sorbents will show significantly increased net sulfur sorption and an extended lifetime.



**Figure 3.** TGA results for Regeneration Test of K57. At regeneration temperatures  $\geq 600^\circ\text{C}$ , the sorbents gain and release nearly the same amount of sulfur in each segment.

## As/P Sorbent Data

Eltron's proprietary sorbents have also been evaluated as arsenic and phosphorus sorbents. In these tests, small sorbent samples (approximately 3.5 mL) were pre-reduced at 300°C for 1 hour in  $\text{H}_2$  and then exposed to arsenic ( $\text{As}_4$ ) and phosphorus ( $\text{P}_4$ ) vapors for 3 hours. The  $\text{As}_4$  and  $\text{P}_4$  vapors were generated by heating elemental arsenic and phosphorus in separate quartz crucibles. Exposure coupons were used both before and after the sorbent test bed in order to gauge the effectiveness of the sorbents in protecting easily poisoned nickel films. Coupons were prepared at Eltron from un-plated stainless steel VCR filter gaskets (Swagelok<sup>®</sup>) with a thin nickel coating ( $\approx 100$  nm) applied to the front surface of the filter element. Initial and final masses were recorded for both the upper and lower coupons and the sorbent material. TGA data is used to estimate the expected mass loss due to pre-reduction. Appropriate evaporation temperatures were determined experimentally for As (525°C) and

P (450°C). These temperatures result in time-weighted average concentrations of 420 ppmv (As<sub>4</sub>) and 250 ppmv P<sub>4</sub> throughout the 3-hour exposure period.

Eltron sorbent K57 strongly bound both arsenic and phosphorus with a total mass gain of nearly 5% in a 3-hour exposure test. Sorbent K59 was less successful in removing As, but showed increased P removal as compared to sorbent K57. Further analysis via Energy Dispersive Spectrometry (EDX) indicates that both arsenic and phosphorus were trapped by both sorbents (see Table 4).

**Table 4.** As and P Sorption Results

Sorbent	Total Weight Gain (%)	Elemental Analysis by EDX	
		As (wt%)	P (wt%)
K57	4.52	4.5	1.6
K59	0.82	2.2	2.5

## References

- [1] U.S. Department of Energy, Office of Fossil Energy and National Energy Technology Laboratory, Hydrogen from Coal Program for the Period 2008 through 2016, September 2008, p. 36.
- [2] Energy Information Administration, Office of Integrated Analysis and Forecasting, U.S. Department of Energy, *International Energy Outlook*, [www.eia.doe.gov/oiaf/ieo/index.html](http://www.eia.doe.gov/oiaf/ieo/index.html).
- [3] W. Surdoval, *Welcome and SECA Overview*, Presentation at the 9<sup>th</sup> Annual SECA Workshop, Pittsburgh, Pennsylvania, Sheraton Station Square, August 5–7, 2008.
- [4] M.V. Mundschau, X. Xie, C.R. Evenson IV, and A.F. Sammells, *Advances in Hydrogen Separation Membrane Technology for the Separation of CO<sub>2</sub> and the Purification of Hydrogen Produced from Coal*, in: Proceedings of the 30<sup>th</sup> International Technical Conference on Coal Utilization and Fuel Systems, April 17–21, 2005, Clearwater, FL.
- [5] D. A. Gribble, Jr., S.L. Rolfe, and M.V. Mundschau, *Perovskite Sorbents for Warm-Gas Removal of Sulfur*, Proceedings of the Twenty-Sixth Annual International Pittsburgh Coal Conference, Pittsburgh, Pennsylvania, September 20–23, 2009, Session: Gasification: Synthesis Gas Cleaning, September 22, 2009.
- [6] J.P. Trembly, R.S. Gemmen, D.J. Bayless, The Effect of IGFC Warm Gas Cleanup System Conditions on the Gas-Solid Partitioning and Form of Trace Species in Coal Syngas and Their Interaction with SOFC Anodes, *Journal of Power Sources* 163 (2007) 986–996, doi: 10.1016/j.jpowsour:2007.10.020.
- [7] D.S. Jack, “Effective Utilization of Hydrogen Membranes for CO<sub>2</sub> Capture,” The Clearwater Clean Coal Conference, May 31-June 4, 2009.
- [8] U.S. Department of Energy, *Cost and Performance Baselines for Fossil Energy Plants*, DOE/NETL-2007/1281.
- [9] A.A. Vierheilig, R.P. Gupta and B.S. Turk, *Attrition Resistant, Zinc Titanate-Containing, Reduced Sulfur Sorbent and Methods of Use Thereof*, U.S. Patent, 7,067,093 B2, Jun. 27, 2006.
- [10] R. Gupta, B. Turk, M. Lesemann, J. Schlather and D. Denton, *Status of RTI/Eastman Warm Gas Clean-up Technology and Commercialization Plans*, Presentation at the Gasification Technologies Conference, October 5–8, 2008, Washington, D.C.