Mitigation of Syngas Cooler Plugging and Fouling

Final Report

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ABSTRACT

This Final Report summarizes research performed to develop a technology to mitigate the plugging and fouling that occurs in the syngas cooler used in many Integrated Gasification Combined Cycle (IGCC) plants. The syngas cooler is a firetube heat exchanger located downstream of the gasifier. It offers high thermal efficiency, but its' reliability has generally been lower than other process equipment in the gasification island. The buildup of ash deposits that form on the fireside surfaces in the syngas cooler (i.e., fouling) lead to reduced equipment life and increased maintenance costs. Our approach to address this problem is that fouling of the syngas cooler cannot be eliminated, but it can be better managed. The research program was funded by DOE using two budget periods: Budget Period 1 (BP1) and Budget Period 2 (BP2).

The project used a combination of laboratory scale experiments, analysis of syngas cooler deposits, modeling and guidance from industry to develop a better understanding of fouling mechanisms and to develop and evaluate strategies to mitigate syngas cooler fouling and thereby improve syngas cooler performance. The work effort in BP 1 and BP 2 focused on developing a better understanding of the mechanisms that lead to syngas cooler plugging and fouling and investigating promising concepts to mitigate syngas cooler plugging and fouling. The work effort focused on the following:

- analysis of syngas cooler deposits and fuels provided by an IGCC plant collaborating with this project;
- performing Jet cleaning tests in the University of Utah Laminar Entrained Flow Reactor to determine the bond strength between an ash deposit to a metal plate, as well as implementing planned equipment modifications to the University of Utah Laminar Entrained Flow Reactor and the one ton per day, pressurized Pilot Scale Gasifier;
- performing Computational Fluid Dynamic modeling of industrially relevant syngas cooler configurations to develop a better understanding of deposit formation mechanisms;
- performing Techno-Economic-Analysis for a representative IGCC plant to investigate the impact on plant economics, in particular the impacts on the Cost of Electricity (COE), due to plant shutdowns caused by syngas cooler plugging and fouling and potential benefits to plant economics of developing strategies to mitigate syngas cooler fouling; and
- performing modeling and pilot scale tests to investigate the potential benefits of using a sorbent (fuel additive) to capture the vaporized metals that result in syngas cooler fouling.

All project milestones for BP 1 and BP 2 were achieved. DOE was provided a briefing on our accomplishments in BP1 and BP2 and our proposed plans for Budget Period 3 (BP 3).

Based on our research the mitigation technology selected to investigate in BP 3 was the use of a sorbent that can be injected into the gasifier with the fuel slurry to capture vaporized metals that lead to the deposit formation in the syngas cooler. The work effort proposed for BP 3 would have focused on addressing concerns raised by gasification industry personnel for the impacts on gasifier performance of sorbent injection, so that at the end of BP 3 the use of sorbent injection would be at "pre-commercial" stage and ready for use in a Field Demonstration that could be funded by industry or DOE. A Budget Continuation Application (BCA) was submitted to obtain funding for BP3 DOE but DOE chose to not fund the proposed BP3 effort.

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1.0 EXECUTIVE SUMMARY

The US Department of Energy (DOE) National Energy Technology Laboratory (NETL) has been facilitating the development of future zero-emissions, high-efficiency polygeneration plants. For these plants, gasification is a key process. To obtain higher overall plant efficiency many plant designs use a firetube heat exchanger, termed the syngas cooler (SC), located between the gasifier and other downstream equipment.

The SC offers high thermal efficiency, but the reliability of the SC has generally been lower than other process equipment in the gasification island due to ash deposits that lead to plugging and fouling of the SC tube inlets. The Wabash River Integrated Coal Gasification Combined Cycle (IGCC) plant (E-Gas gasification technology) and the Polk Station IGCC plant (GE gasification technology) exhibit similar plugging/fouling problems in the SC despite having different operating conditions (see Figure 1). The plugging/fouling results in plant shutdowns to clean the system that adversely impact plant economics – in particular the cost of electricity. Substantial progress has been made on this problem since the plants were built in the 1990's, but further improvement is needed. These first-of-a-kind IGCC plants struggle to operate for more than 60 days between plant shutdowns. For gasification systems to be commercially viable for polygeneration plants they will likely need to operate continuously on a "24x7" basis for 8,000 hours/year as per other fired equipment used in the chemical process plants.


Source – Global Energy, Inc

Figure 1. Examples of tube sheet fouling at Wabash River IGCC plant (left) [Guenther et al. 2011] and Polk Station IGCC plant (right) [McDaniels and Hornick, 2002].

Through funding from the DOE, Reaction Engineering International (REI), with assistance from the University of Utah (UofU), investigated strategies to mitigate SC plugging and fouling. We had active collaboration with the gasification industry throughout the project.

- A coal gasifier original equipment manufacturer (OEM) that operates and develops IGCC plants has collaborated with the project and provided cost share to the project.
- An IGCC plant that uses a gasifier developed by the above referenced OEM has provided information and deposit samples from their SC.

- The Aurora^{TM} sorbent support team at Imerys, developer and provider of the Aurora^{TM} sorbent, provided information, insights and the sorbent material used in pilot-scale tests performed within the project.
- Reliance Industries Limited (RIL), owner of the worlds' largest refinery and petrochemical complex which is developing the worlds' largest gasification plant (10 next generation gasifiers with 10 syngas coolers), provided insights and guidance into concerns about syngas cooler performance from a refinery perspective.

Key Findings and Accomplishments

In the following are described the key findings and accomplishments from our research.

1. Impacts on Plant Economics

Modeling performed by REI using the DOE Lifetime Cycle Analysis Tool (LCAT) software clearly shows that plant availability has the largest impact on plant economics – in particular on Cost of Electricity (COE). A mitigation strategy that can increase plant availability by about 8% (i.e., eliminate 1 shutdown every two years) is predicted to reduce the COE by 5%.

2. SC Deposit Analysis

Data from laboratory analysis of SC deposits shows that the mechanism for deposit formation in a SC and a coal fired boiler are quite different, resulting in deposits with very different structure and composition. Furthermore, the temperature in a SC is well below typical ash sticking temperatures.

- In a boiler, deposits form due to partially melted particles impacting on walls or surface condensation of readily vaporizable minerals, followed by sintering of the deposited material.
- In a SC, the deposits consist of fume particles that deposit on surfaces and are held in place by forces that act on small particles (i.e., van der Waals and electrostatic forces) that subsequently sinter.

Laboratory analyses of SC deposits demonstrated:

- SC deposits have a fairly uniform composition regardless of where along the syngas flow path the deposits are collected;
- SC deposits do NOT have an initiation layer such as occurs for coal fired boiler deposits;
- Three main phases are observed in the SC deposits: Calcium aluminosilicates; Sulfide rich species; and Vanadium rich species;
- SC deposits consist mainly of fine (< 1 μm) and fine-to-small (< 5 μm) spherical particles that appear to sinter and diffuse over time to create strong, tenacious deposits; and
- Char particles (10-20 μm) are rarely observed on the gas side surface of the SC deposit.

3. Deposit Formation Hypothesis

A hypothesis for deposit formation was developed based on data from the SC deposit analyses. Note that little, if any, deposition occurs within the tubes of the SC and the temperatures in the SC region are generally below the typical ash sticking temperature. The small particle diameter of the fume is the dominant reason for the particles to deposit and remain at a surface. Our hypothesis for deposit formation is highlighted below:

1) Metals and material contained in the ash of the solid fuel vaporizes or is otherwise released during devolatilization when exposed to the high temperatures in the gasifier. Most of the ash in petcoke is organically associated and thus readily vaporizes at high temperatures [Linak et al., 2004].
2) The vaporized material forms a submicron-sized fume through condensation and homogeneous nucleation. Particle growth continues as the hot syngas travels through the system. The relatively long residence time in the gasifier promotes growth of the average particle size of the fume.
3) The sub-micron particulate in the fume and small ash particles deposit onto flowfield stagnation points in the syngas cooler region. Deposition is caused by particulate impacting onto the surfaces. The particulate remains in-place due to forces that act on small particles (i.e., electrostatic and van der Waal forces).
4) Deposited particulate undergo solid-state diffusion and sinter over time, giving the deposits high structural strength. The melting point of some of the species may be near or lower than syngas cooler temperatures.

4. Sorbents to Capture Vaporized Metals – Modeling and Pilot Scale Tests

Modeling:

Published laboratory data demonstrates that sorbents and limestone can be used to capture (remove) from the syngas the “bad actor” species that lead to fouling deposits (i.e., metal sulfides, vanadium, sodium) [Gale and Wendt, 2005], [Kang et al., 2012], [Linak et al., 2004]. Hence, REI performed thermodynamic equilibrium calculations to investigate the effectiveness of two sorbents, limestone and kaolinite, to capture the “bad actor” species. Assuming a two stage gasifier, three injection locations were evaluated: (1) directly into Stage 1 (e.g., with the slurry feed or recycled char); (2) into the transition section between Stage 1 and Stage 2; and (3) at the Stage 2 exit.

Model results indicated that both sorbents are effective for removing sulfides and vanadium species from the syngas.

- Limestone is well suited for capturing sulfur and was more effective for “upstream” injection into Stage 1.
- Kaolinite is good for capturing sodium and vanadium and was more effective for “downstream” injection, such as at the transition section between Stage 1 and Stage 2.

Pilot Scale Tests:

Based on the literature data and model results REI performed pilot scale tests at the UofU to demonstrate the effectiveness of Aurora^{TM}, a commercially available sorbent (fuel additive) that has been demonstrated in petcoke and coal fired industrial systems to mitigate fouling and deposit formation [Landon and Perronnet, 2014]. The tests were performed in a reactor used for fundamental studies of aerosol formation due to coal firing. The reactor uses special purpose probes that provide accurate data for particulate ranging in size from < 1µ to 20µ. The sorbent was co-fed with the fuel to better simulate the conditions that would occur in a gasifier.

- The test results demonstrated that the Aurora™ sorbent is very effective at capturing vaporized metals. For all of the tested sorbent addition rates a very large reduction in particles was observed. Submicron particulate was reduced by > 90% on a mass basis. Particles in the range of 1-19 µm were reduced by about 50% on a mass basis.
  - The lowest sorbent dosage tested was 0.6wt% of the solid fuel feed (i.e., 2X the wt% of ash in the solid fuel feed).
  - Literature data indicates lower sorbent dosages can provide effective metals capture.
- TGA data for processing the used sorbent material from the OFC tests at a high temperature (1500C) showed < 3% weight loss during reheat indicating only a small amount of the captured fume material would be re-breleased. .

5. CFD Modeling of SC Geometries

A parametric CFD modeling study using in-house tools was performed by REI to better understand deposition in a SC and to investigate mitigation strategies. The study involved varying numerical parameters contained in the model, syngas conditions (particulate flow-rate and particulate size/spatial distribution), syngas cooler geometry (tube ID, tube inlet size/shape [straight vs. funneled inlet]) and upflow versus downflow SC orientation.

Initial multiphase CFD modeling results were performed using a deterministic, particle cloud model that had been used successfully in numerous studies of deposition issues in coal fired electric utility boilers was not able to predict the deposition of the fine particulate contained in the fume. With the deterministic model the fine particulate follows the gas flow and thus cannot deposit on a surface. Hence, a Stochastic Separated Flow (SSF) particle model was developed and implemented into the CFD model. As per the deterministic particle cloud model the SSF model uses a Largrangian framework. With the SSF model the particle trajectories involves the instantaneous fluid velocity instead of the mean velocity for particle momentum transfer equation. Using the SSF model the fine particles need not follow the gas flow and thus can deposit on surfaces. In addition, the SSF model allows particle trajectories to split into different tubes of the SC.

The CFD simulations using the SSF model predicted that deposits concentrate near tube inlets and at distinct stagnation lines near tube inlets and little (if any) deposition a few tube diameters after the tube inlet. These findings are in agreement with field observations reported by plant and industry personnel that deposits buildup around tube inlets, forming shapes described as “elephant trunks”, “clam shells” and “Sydney Opera Houses” and that there is rarely any fouling within the SC tubes.

2.0 RESULTS AND DISCUSSION

In this section are provided further details on the work effort and accomplishments during BP1 and BP2 of the project. As noted above, BP3 of the project was not funded. The discussion below is organized by the Task within the project for which the work effort was performed.

Task 1.0 Project Management, Planning and Reporting

Objective: Coordinate and Manage the Work Effort

This Task included all the work elements required to maintain and revise the Project Management Plan, to manage and report on activities in accordance with the plan and included the necessary activities to ensure coordination and planning of the project with DOE/NETL and other project participants. The project schedule is shown in Figure 2 and the Project Milestones and their status are listed in Table 1.

- REI negotiated and signed a cooperative agreement with the DOE for this project. The documents for the Project Management Plan, Technology Transfer Plan, project budget information and Data Rights were updated and accepted by DOE. A subcontract between REI and the UofU was negotiated and signed. As per their request, no subcontract was executed between REI and the OEM that collaborated with this project and provided in-kind cost share to the project.
- The project kick-off meeting was held in January 5, 2012. The Principal Investigator traveled to the DOE-NETL facility in Morgantown, WV to participate in the kick-off meeting. The presentation was performed as a web conference. Meeting participants included personnel from DOE-HQ, the Morgantown and Pittsburgh DOE-NETL sites, project team members from the recipient, the UofU and personnel from the gasification industry OEM that collaborated with this project.
- *Advanced Energy Systems Peer Review:* REI participated in the 2012 Advanced Energy Systems Peer Review held April 23-27, 2012 in Morgantown, WV. The review was part of NETL's Strategic Center for Coal (SCC) bi-annual Peer Review of all programs contained in its portfolio. In FY12, Gasification and Turbine projects in the Advanced Energy Systems (AES) portfolio and supporting technology development activities are being reviewed, which includes the project described in this report. The Peer Review was conducted by the American Society of Mechanical Engineers (ASME). REI provided the DOE designated points of contact with all requested information, forms and documents in the requested formats. Considerable detail was included in the Project Information File (PIF) and in the Peer Review presentation material.
    - Three members of the REI-UofU project team and one member of the technical staff from the OEM from the gasification industry that collaborated with this project traveled to Morgantown, WV to provide a presentation to the Peer Review panel on April 26, 2012. The 45-minute presentation described the motivation, goals, methods, assumptions, current findings and future plans for this project. The presentation was followed by (about) a 30-minute question and answer session.

	Task	Lead	BP 1				BP 2										BP3			
			q1	q2	q3	q4	q1	q2	q3	q4	q5	q6	q7	q8	q9	q10	q1	q2	q3	q4
1	Management & Planning & Reporting	REI																		
	1. Set up contracts with DOE and all sub-contractors	REI	x																	
	2. Conduct project kick-off meeting	REI	x																	
	3. Conduct regular project review	REI	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
	4 Provide DOE with required quarterly reports and forms	REI	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
	5. Provide DOE annual topic report, property report, papers, forms	REI				x				x				x						x
	(1) submit continuation application for next BP	REI			**M**											**M**				
	6. Submit annual incurred cost proposal to DCAA	REI			x				x				x						x	
	7. Provide annual technical briefing to DOE PM	REI				**M**							**M**							**M**
	8. Submit Final Technical and Financial Reports to DOE	REI																		**M**
	9. Select technology to validate in BP3	REI										**M**								
	10. Add Syngas Cooler OEM to project team	REI										**M**								
2	Deposit – collection & Analysis	REI																		
	1. Analyze IGCC SC deposits and SC plugging samples	OEM		x				x												
	2. Develop map of deposits in IGCC SC region	OEM		x				x												
	3. Characterize deposits from UofU lab tests	REI							x											
3	Laboratory Experiments	UofU																		
	1. Update Experiment Plan	UofU	**M**		x		x		x											
	2. Modify UofU 1 tpd pilot scale gasifier and perform tests in it	UofU	x	x	x															
	3. Deposit Bond Strength Tests (impinging jet)	UofU																		
	(1). Ash generated in LEFR	UofU		x	x	x				x										
	(2) Ash generated in gasifier	UofU				x	x	**M**	x	x										
	(3) Ash from ground SC deposit	UofU			x	x	x	x	x											
4	Modeling	REI																		
	1. Support Test Design, Data Interpretation	REI	x	x	x	x	x	x	x	x										
	2. Heat, Mass Balance Calculations to Provide Inputs For Detailed Modeling to Evaluate SC Fouling and Plugging	OEM	x		x		x		x											
	3. Investigate SC Deposition and Plugging	REI	x	x	**M**	x	x	x	x	x										
	4. Investigate Strategies to Mitigate Fouling and Plugging	REI			x	x			**M**	x										
	5.Validate CFD deposition model	REI								x	x	**M**								
	6. Determine adhesive bond strength of deposit	REI								x	x	**M**								
5	Economic evaluation and impact on COE of SC improvements	OEM				x				x										
6	Validation of Selected Technology	REI															x	x	x	**M**

Note:
1. x = project activity
2. **M** = milestone
3. REI = Reaction Engineering International
4. UofU = University of Utah
5. OEM = original equipment manufacturer from the gasification industry collaborating with project.
6. SC = syngas cooler
7. BP3 = not currently funded. Decision on BP3 funding to be determined at end of BP2. Tasks, schedule and milestones for BP3 not fully developed at this time and will be refined in future revisions of PMP at end of BP1 and BP2

Figure 2. Project Tasks and Schedule for BP1–BP2 and original plan for BP3.

Table 1. Milestone Status Report

Budget Period	ID	Task No.	Milestone Title	Milestone Description	Planned Completion Date	Actual Completion Date	Verification Method	Comments
BP1	1	3	UofU Laboratory Scale Experiments	Update experiment test plan	12/31/2011	12/31/2011	Test plan provided & reported	**COMPLETED**
BP1	2	4	Modeling	CFD model results for SC deposition and plugging for 10 scenarios.	6/30/2012	6/30/2012	Results provided & reported	**COMPLETED**
BP1	3	1	Project management, planning and reporting	Provide annual technical review to DOE project officer at NETL	9/30/2012	9/18/2012	Meeting provided	**COMPLETED**
BP1	4	1	Project management, planning and reporting	Submit continuation application for BP2	6/30/2012	6/30/2012	Application submitted	**COMPLETED**
BP2	5	3	UofU Laboratory Scale Experiments	Deposit Bond Strength test using Ash from Gasifier - 8 sample bags collected in gasifier and 16 LEFR tests completed with collected samples.	3/31/2013	6/30/2013	Samples collected, tests performed and data reported	**COMPLETED. Completion Date slipped due to an equipment failure**
BP2	6	4	Modeling	CFD model results for strategies to mitigate SC plugging and fouling for 5 scenarios.	6/30/2013	6/30/2013	Results provided & reported	**COMPLETED**
BP2	7	1	Project management, planning and reporting	Select mitigation technology to validate in BP3	3/31/2014	3/31/2014	Selected technology identified & reported	**COMPLETED**
BP2	8	1	Project management, planning and reporting	Provide annual technical review to DOE project officer at NETL	3/31/2014	4/24/2014	Meeting provided	**COMPLETED**
BP2	9	1	Project management, planning and reporting	Submit continuation application for BP3	3/31/2014	12/23/2014	Application submitted	**COMPLETED (Submitted by 1-30-15)**
BP2	10	4	Modeling	AES-1 Validate CFD deposition model versus laboratory quality data	3/31/2014	3/31/2014	Data provided and reported	**COMPLETED**
BP2	11	1	Project management, planning and reporting	AES-2 Add a syngas cooler manufacturer to the project team	3/31/2014	1/31/2014	OEM added to team	**COMPLETED**
BP2	12	4	Modeling	AES-3 Quantify the ash adhesion strength	3/31/2014	3/31/2014	Data provided and reported	**COMPLETED**
BP3	10	6	Validation	Perform test to validate mitigation technology	9/30/2014		Data provided and reported	**BP3 Not Funded**
BP3	11	1	Project management, planning and reporting	Provide annual technical review to DOE project officer at NETL	10/30/2014		Meeting provided	**BP3 Not Funded**
BP3	12	1	Project management, planning and reporting	Submit Final Report and all contractually required forms and reports to DOE	12/31/2014		Report submitted	**BP3 Not Funded**

- Project meetings involving REI and the UofU were held on a periodic basis (typically via conference call). Project meetings (via conference call) involving REI and the OEM were held about every two months; the UofU participated (as needed) in meetings/communications with the OEM if questions about UofU laboratory testing were to be discussed. Project briefings with the IGCC plant collaborating with this project were provided on a roughly annual basis.
- Technical project briefings were provided to the DOE Project Officer on an annual basis, with additional informal briefings provided when requested.
- All contractually required reports and forms were provided by REI to DOE in the appropriate format as needed.
- During each year of the project REI prepared and submitted an Annual Indirect Cost Proposal to our cognizant agency, the Defense Contract Audit Agency (DCAA).
- As per the cooperative agreement, REI submitted a Budget Continuation Application (BCA) to justify funding for BP2 of this project. The BCA was submitted approximately 90 days prior to the end of BP1. Included in the application was a DRAFT Annual Topical Report describing the goals, methods, assumptions, findings, results and accomplishments for this project during BP1 of this project. The BCA was approved and funding for BP2 provided.
- *No-Cost Time Extensions:* Prior to the end of BP2, REI requested and was granted a six month no-cost time extension that extended BP2 from September 30, 2013 to March 31, 2014 and extended BP3 (if funded) from September 30, 2014 to March 31, 2015. After the Technical Briefing provided by REI to DOE on April 24, 2014, REI requested and was granted a three month no-cost time extension that extended BP2 from March 31, 2014 to June 30, 2014 and extended BP3 (if funded) from March 31, 2015 to June 30, 2015. REI subsequently requested and was granted a three month no cost time extension for BP2 that extended BP2 from June 30, 2014 to September 30, 2014. REI subsequently requested and was granted a six month no cost time extension for BP2 that extended BP2 from September 30, 2014 to March 31, 2015, with the stipulation that a BCA to request funding for BP3 be submitted to DOE by January 31, 2015.
- *Mitigation Technology To Validate in Budget Period 3:* Based on the results of modeling, experiments, literature reviews and discussions with industry personnel REI selected sorbent injection as the mitigation technology to pursue in BP3 (if funded). Sorbent injection allows capturing the vaporized metals in the syngas that cause the SC fouling. Discussions were held with personnel from the OEM collaborating with this project and with IGCC plant personnel to determine what information would be needed by the plant to allow this project to perform a field test of sorbent injection in their SC. The results of these discussions were used to formulate the proposed BP3 work plan. The OEM and the IGCC plant had both been involved in previous field tests of new technologies and emphasized that the mitigation technology used in the field test not create other operational problems for the SC or other processes at the plant. The perceived risk by IGCC plant personnel for performing a field test and the amount of technical support to be provided by the plant were important aspects of the criteria for selecting a technology.
- As per the cooperative agreement, REI submitted a Budget Continuation Application (BCA) to obtain funding for BP3 of this project. The BCA was submitted approximately 90 days prior to the end of BP2. The requested funding was not approved and thus BP3 was not performed.

Milestone Status

All project milestones for BP1 and BP2 have been completed.

- *Milestone #1 – Update UofU Test Plan:* During the project the UofU routinely updated the Test Plan for the laboratory scale experiments they performed for this project. They maintained a 6-month "look-ahead" test plan to ensure all needed materials would be available on-time to perform the tests.
- *Milestone #2 – CFD Modeling of SC Deposition.* REI provided to DOE a Technical Note documenting the modeling performed to complete this milestone.
- *Milestone #3 – Provide Annual Technical Review to DOE.* REI provided via conference call the required technical briefing prior to the end of BP1.
- *Milestone #4 – Submit Budget Continuation Application for BP2.* REI submitted the BCA on-time and was granted funding for BP2.
- *Milestone #5 - UofU Laboratory Scale Experiments* - was not completed on schedule due to an equipment failure. As noted in Table 1 this milestone completed during next quarter. For this milestone the UofU modified the UofU high pressure, 1 tpd pilot scale gasifier to operate in a manner to simulate the second stage of a two stage gasifier. The pump used for the Stage 2 injector that failed was replaced. After replacing the pump, the gasifier was successfully operated as a two stage gasifier, ash samples captured in the downstream filter and adhesion bond strength tests performed in the LEFR using the ash material captured in the gasifier filter.
- *Milestone #6 – CFD Modeling of Mitigation Strategies* – CFD modeling results for a variety of syngas cooler geometry changes as well as CFD modeling results for use of a soot blower based mitigation strategy were described in a Topical Report submitted to DOE.
- *Milestone #7 – Select Mitigation Strategy to Validate in BP3* – REI selected injecting a kaolinite based sorbent (fuel additive) into the gasifier to capture the vaporized metals that cause the buildup of fouling deposits in the SC region.
- *Milestone #8 – Provide Annual Technical Review to DOE Project Officer.* Due to schedule conflicts DOE agreed to perform the briefing on April 24, 2014. As a result of the briefing, REI requested a no-cost extension to have additional time to prepare the BCA needed for the BP3 funding request.
- *Milestone #9 – Submit BCA for BP3* – The BCA request to obtain funding for BP3 was submitted on time but DOE chose to not fund the proposed BP3 effort.
- *Milestone #10 - CFD Based Deposition Model Validation:* The work effort to validate our CFD based deposition model to laboratory quality data obtained in tests performed at the UofU was completed on-schedule. The comparison showed very good agreement between predicted and measured deposition rates. Further details on the experiments and modeling performed are provided in Sections 3.0 and 4.0, respectively. This satisfied Action Item AES-1 from our AES review.
- *Milestone #11 - Syngas Cooler OEMs:* REI held discussions and shared data from this project with two syngas cooler OEMS. Involving a syngas cooler OEM in the project satisfied Action Item AES-2 (Milestone #11) from our AES review.
- *Milestone#12 - Deposit Strength Validation:* REI developed estimates of the adhesion bond strength between deposits and the surface to which the deposit is attached. Further details are provided in Section 3.0. and 4.0 This satisfied Action Item AES-3 from our AES review.

Technology Transfer

Findings from the research performed for this project were described to the gasification and engineering community through presentations at technical conferences and meetings with gasification industry personnel. Participation in these conferences provided for interaction with personnel ranging from gasification plant operators to researchers from academia and the gasification industry and provided the opportunity to highlight our expertise at addressing complex operational issues for solid fuel gasification to an audience with great interest in the topic.

- Bockelie, M.J., Davis, K.A., Fry, A.F., Denison, M.K., Shurtz, T., Wang, D., Whitty, K., Celebi, M.C., Jaramillo, C., Wendt, J.O., "Toward A Technology To Mitigate Syngas Cooler Plugging and Fouling", *Proceedings of the International Pittsburgh Coal Conference 2012*, Pittsburgh, PA, October 15-18, 2012.
- Bockelie, M.J., Celebi, M.C., Davis, K.A., Denison, M.K., Jaramillo, C., Fry, A., Pummill, R., Shurtz, T., Wang, D., Wendt, J.O., and Whitty, K., "Toward A Technology To Mitigate Syngas Cooler Plugging and Fouling", *The 9th Asia-Pacific Conference on Combustion (ASPACC),* Gyeongju, Korea, May 19-22, 2013.
- Bockelie, M.J., Davis, K.A., Denison, M.K., Pummill, R., Wang, D., Wendt, J.O., Celebi, M.C., Waind, T., Jaramillo, C., Fry, A., and Whitty, K., "Toward A Technology To Mitigate Syngas Cooler Plugging and Fouling", *The 38th International Technical Conference on Clean Coal & Fuel Systems,* Clearwater, Florida, June 2-6, 2013.
- Bockelie, M.J., Davis, K.A., Denison, M.K., Wang, D., Pummill, R., Shim, H., and Wendt, J.O., "Mitigation of Syngas Cooler Plugging and Fouling", *Poster - Gasification Technologies Council 2013 conference*, Colorado Spring, Colorado, October 13-16, 2013.
- Bockelie, M.J., Davis, K.A., Pummill, R.,, Wang, D., Wendt, J.O., Can Celebi, M., Fry, A., Jaramillo, C., Waind, T., Whitty, K.,, "Mitigation of Syngas Cooler Plugging and Fouling", *The 39th International Technical Conference on Clean Coal & Fuel Systems,* Clearwater, Florida, June 2-5, 2014
- Bockelie, M.J., Davis, K.A., Pummill, R.,, Denison, M.K., Shurtz, T., Wang, D., Whitty, K., Can Celebi, M., Fry, A., Jaramillo, C., Zhongua, Z., and Wendt, J.O., "Mitigation of Syngas Cooler Plugging and Fouling", *Proceedings of the International Pittsburgh Coal Conference 2014,* Pittsburgh, PA, October 6-9, 2014.
- Bockelie, M.J., Davis, K.A., Pummill, R.,, Denison, M.K., Shurtz, T., Whitty, K., Can Celebi, M., Fry, A., Jaramillo, C., Zhongua, Z., and Wendt, J.O., "Mitigation of Syngas Cooler Plugging and Fouling", *To be presented at the International Pittsburgh Coal Conference 2015,* Pittsburgh, PA, October 5-8, 2015.
- Bryers, R. W. Bockelie, M.J., Davis, K.A., Pummill, R.,, Wang, D., Wendt, J.O., Can Celebi, M., Fry, A., Jaramillo, C., Waind, T., Whitty, K.,, "Mitigation of Syngas Cooler Plugging and Fouling", *The 39th International Technical Conference on Clean Coal & Fuel Systems,* Clearwater, Florida, June 2-5, 2014.
- Celebi, M.C. and Whitty, K.J., "Characterization of Fine Particulate Material from Syngas in a Pilot Scale Entrained Flow Oxygen Blown Coal Gasifier During Two Stage

Gasification," *Presented at the International Pittsburgh Coal Conference 2014,* Pittsburgh, PA, October 6-9, 2014.

In addition:

- REI conducted site visits in 2011 and 2013 to an IGCC plant collaborating with this project to tour the plant, share the results from our research with the plant engineering staff and senior managers and to discuss proposed work effort to be performed in BP3;
- REI held discussions with Reliance Industries, Ltd (RIL) in India on their concerns about syngas cooler fouling, potential mitigation strategies and our proposed work plan for BP3. RIL owns the worlds' largest refinery and petrochemical complex and is developing the worlds' largest gasification plant (10 next generation gasifiers with 10 syngas coolers). The discussions with RIL led to their participation in the proposed BP3 project.
- REI held discussions with NEXAN (Alberta, Canada) about the similarities and differences in fouling deposits they encounter in their syngas coolers due to vaporized metals (Vanadium, Nickel) that occur for gasification of feedstock containing unconventional oil. NEXAN uses a dry feed, entrained flow gasifier that operates at a higher temperature than the E-gas gasifier and uses a different type of syngas cooler design.
- REI held discussions with two syngas cooler OEMs that have a working relationship with the OEM from the gasification industry that collaborated with this project. REI provided an overview of the key findings from this project. Discussions included the advantages and challenges of using a sorbent as well as other potential strategies to mitigate syngas cooler fouling; and
- After being notified by DOE that BP3 would not be funded, REI initiated discussions with Reliance Industries Limited (RIL) about the possibility of performing selected Pilot Scale tests to further investigate the use of sorbent to mitigate syngas cooler fouling.

Task 2.0 Deposit – Collection & Analysis

Objective: Generate structure and chemical composition data for fouling deposits in the SC of an IGCC plant.

Figure 3. Photograph of deposit samples.

In this Task REI has collaborated with an OEM to obtain and analyze samples of the deposits that accumulate in the syngas cooler and in the equipment surrounding the cooler at an IGCC plant (see Figure 3). Altogether, about 25 samples were collected and analyzed. The samples were collected from different locations along the hot syngas path near the SC. Samples were analyzed using a variety of techniques including ICP-MS (inductively coupled plasma with mass spectroscopy), SEM (scanning electron microscopy), SEM-EDX (SEM with energy dispersive x-ray spectroscopy), PCSEM (SEM with point counting). High Resolution Transmission Electron Microscopy (HR-TEM), X-ray mapping, Loss on Ignition (LOI). The fuel (petcoke) was analyzed with ultimate/proximate analysis and the fuel ash was analyzed with , Partial Chemical Fractionation, SEM, SEMPC, Ash elemental, and Ash Fusion Temperature (AFT). Last, Fluxant material was analyzed using SEM, CCSEM, SEMPC, Ash Elemental analysis and AFT was also determined. Some laboratory tests provided more useful information than other laboratory tests. The following summarizes our findings for this Task.

Fuel Ultimate and Proximate Analysis

Ultimate and proximate analyses are standard industry tests that are used to determine the composition of fuels or other materials. By heating the sample in oxidizing conditions and measuring the quantity and composition of the evolved gases the carbon, hydrogen, oxygen, nitrogen, water, sulfur, and ash content of the fuel can be determined. The amount of carbon in volatile form or fixed form can also be determined. Often, the heating value of the fuel is also recorded. These tests were performed on a sample of the petcoke used at the collaborating IGCC plant and on several deposit samples.

Results of the petcoke fuel analyses are presented in Table 2 (ultimate) and Table 3 (proximate) The fuel is a typical petcoke with high amounts of carbon (greater than 80 wt%) and very little ash detected, about 0.3 wt%.

Table 2. Ultimate Analysis - Fuel.

	As Received (wt. %)	Dry Basis (wt. %)
Sulfur	5.89	6.43
Hydrogen	3.12	3.41
Carbon	80.67	88.05
Nitrogen	1.46	1.59
Oxygen	0.18	0.19

Table 3. Proximate Analysis - Fuel

	As Received (wt. %)	Dry Basis (wt. %)
Moisture	8.38	--
Ash	0.30	0.33
Volatile Carbon	9.88	10.78
Fixed Carbon	81.44	88.89
Total	100.00	100.00

The analyses performed on the deposit samples revealed that the deposits are enriched in several metals including vanadium, iron, nickel, and zinc. Relatively high amounts of sulfur were also detected in the samples. SEM-EDX was used to generate elemental maps of sections of the deposits and it was found that areas of high sulfur concentration frequently coincided with regions of high iron or zinc concentration, leading to the conclusion that sulfur is generally found as an iron or zinc sulfide. Other major phases include a vanadium rich phase consisting of vanadium oxides and vanadate species and a phase rich in calcium aluminosilicates (Figure 4).

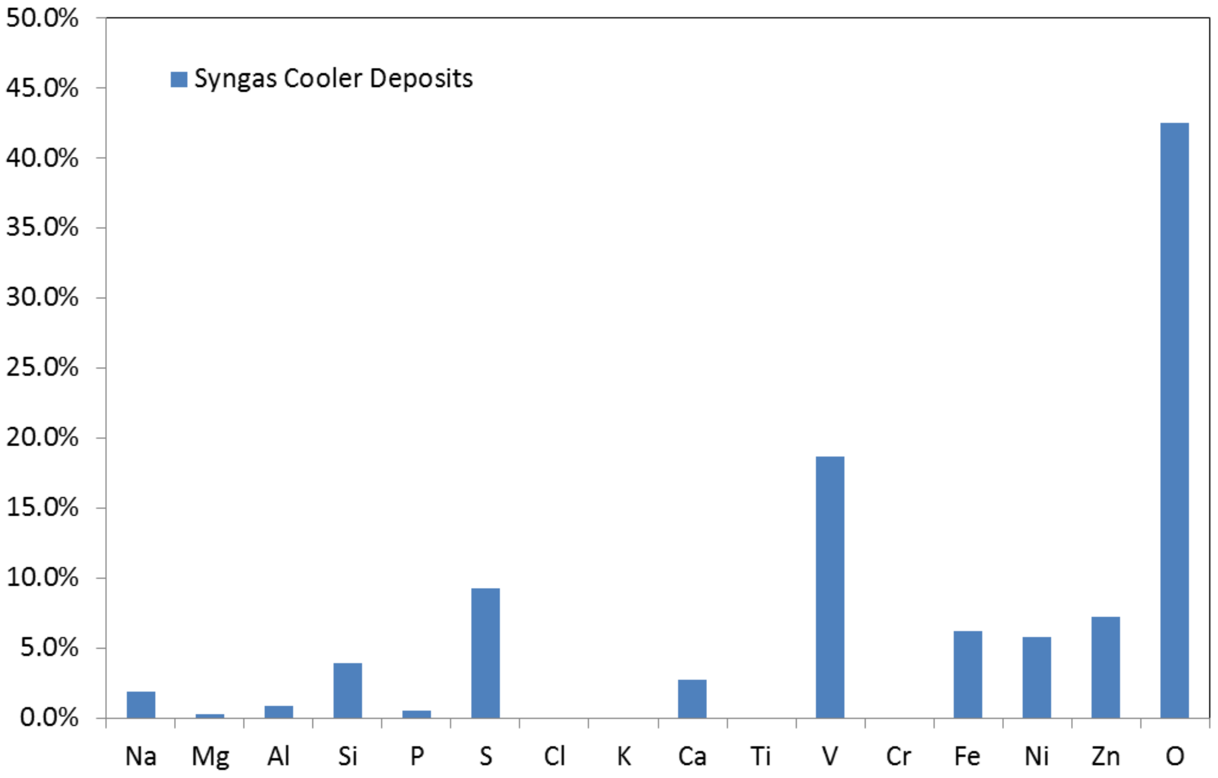
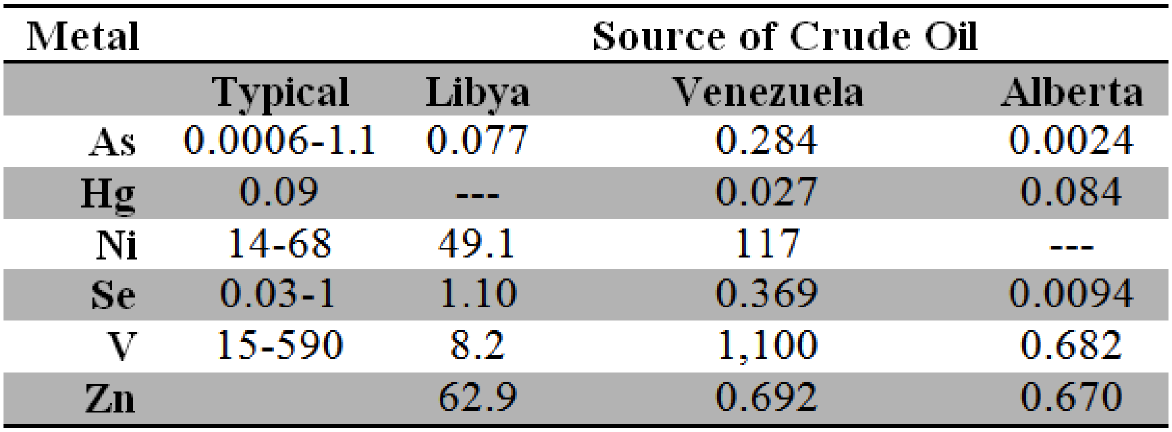


Figure 4. Average elemental composition of the syngas cooler deposits in weight percent on a carbon-free basis.

The high concentration of vanadium and other metals in the deposits is not surprising. Petcoke is an oil-based. In the late 1960's and early 1970's residual fuel oil was a popular fuel until studies showed that it lead to fouling problems due to the presence of vanadium and other metals. The vanadium and many of the other metals are water soluble (i.e., organically bound) and thus are released from the petocke during pyrolysis / devolatilization.

Petcoke is an attractive fuel for an IGCC plant because it is a readily available, inexpensive (waste) fuel with high carbon content and high heating value [Tilmann and Harding, 2001]. The amount of vanadium and other metals in petcoke is higly dependent on the source of the oil used to generate the petcoke. Hence, the fouling factor for petcoke from a refinery can vary significantly depending on the source of the oil the refinery has recently processed (see Figure 5).



Metal	Source of Crude Oil			
	Typical	Libya	Venezuela	Alberta
As	0.0006-1.1	0.077	0.284	0.0024
Hg	0.09	---	0.027	0.084
Ni	14-68	49.1	117	---
Se	0.03-1	1.10	0.369	0.0094
V	15-590	8.2	1,100	0.682
Zn		62.9	0.692	0.670

Figure 5. Metals content of crude oil used to produce petcoke varies by source of the crude oil [Tillman and Harding, 2004].

The analysis shows that the deposits found in a syngas cooler differ from typical boiler deposits in some very significant ways. First, typical boiler deposits will show evidence of a deposit initiation layer made of particles with low melting points or droplets (usually sulfates), but this effect was not observed in syngas cooler deposits. While syngas cooler deposits do show some evidence of layering, the unique chemistry near the root of the deposits indicative of an initiation layer was not detected in the analysis. Rather the syngas cooler deposits appear to be fairly uniform in composition throughout the deposit (Figure 6). Second, the average particle diameter in a syngas cooler deposit is much smaller than for a typical boiler deposit. The syngas cooler deposits had a substantial amount of submicron particulate with an average particle size between 1-2 µm. Typically >99% of the particles had a diameter less than 5 µm (Figure 7).

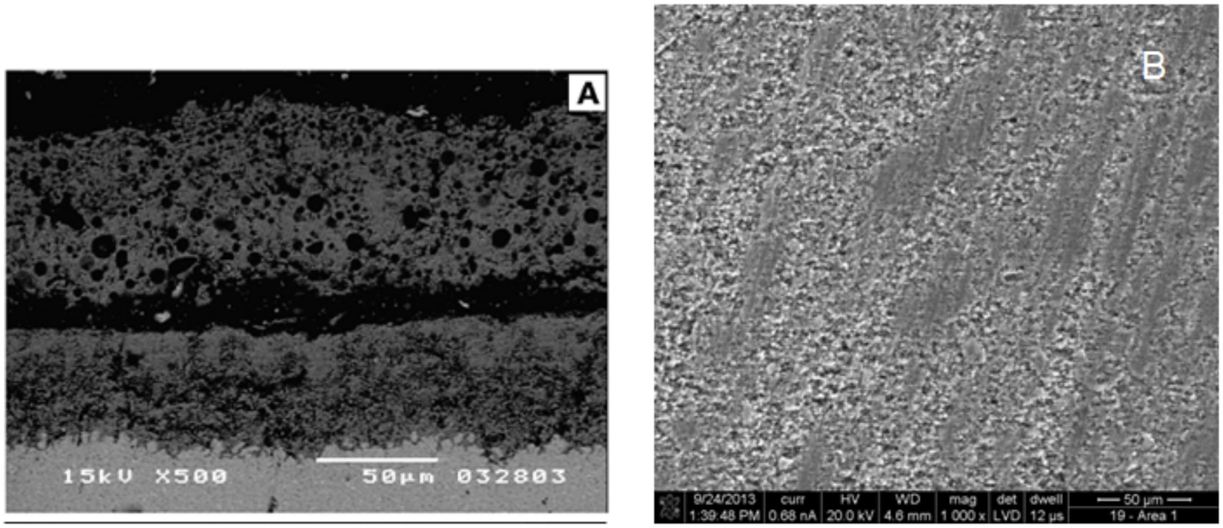


Figure 6. SEM images of a typical PC boiler deposit (A) and an IGCC SC deposit (B). PC boiler deposit shows evidence of an layering and of an initiation layer. A wide range of particle diameters are present in the deposit while the SC deposit is fairly uniform and consists mainly of very fine particles. Streaks in the IGCC deposit are cut marks from sample preparation.

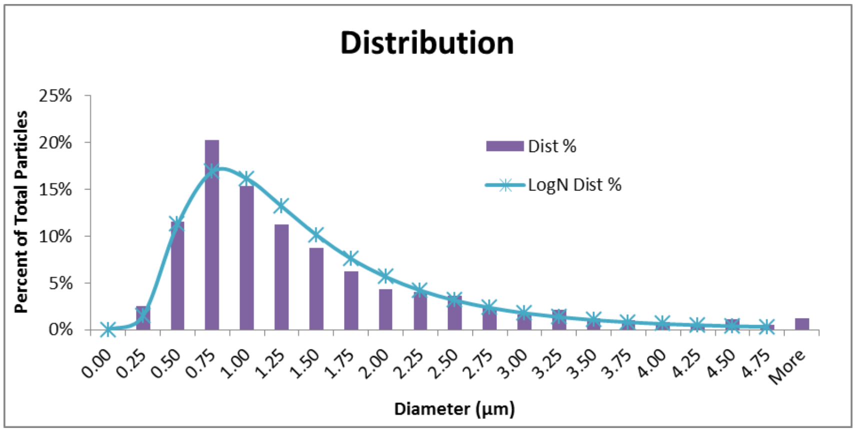


Figure 7. Example particle size distribution of a syngas cooler deposit.

Particle size is important as it provides a clue to the deposit formation mechanism. As particle size decreases, adhesive forces can dominate over disruptive forces, causing particles to cling to surfaces and other particles. In Figure 8, adhesive forces, such as electrostatic attraction and thermophoretic forces, are compared to disruptive forces, such as gravitational and stokes friction as a function of particle size. As the particle size drops below 10 µm the adhesive forces are stronger than the disruptive forces. REI believes this phenomenon is an important contributor to the formation of the SC deposits.

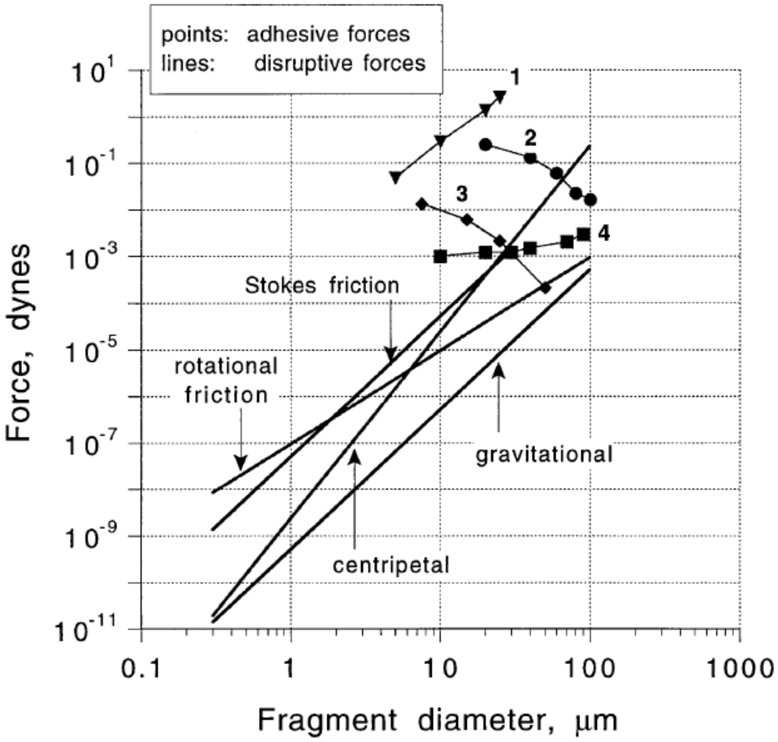


Figure 8. Comparison of adhesive and disruptive forces acting on particles. Image from [Hurt and Davis, 1999].

SEM analysis shows that the particles become less defined over time. Images taken near the leading edge of the samples showed very discrete spherical particles while images taken near the root of the samples show amorphous or crystalline matrices (see Figure 9). The particles undergo solid state diffusion and sintering processes over time, fusing into each other and forming amorphous structures. It is believed that this behavior leads to the increase in deposit strength over time.

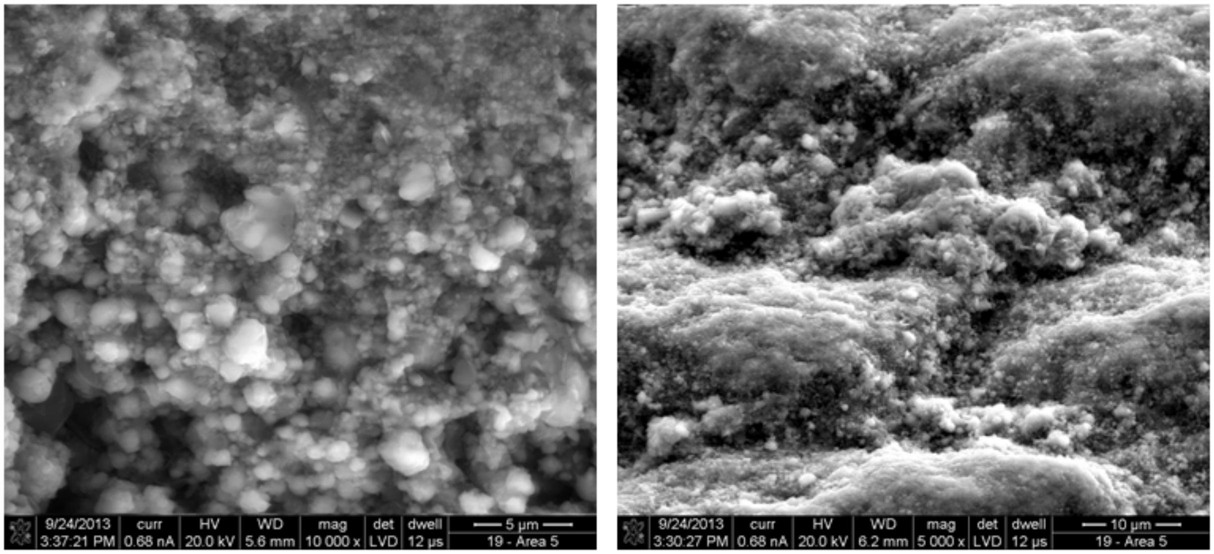


Figure 9. SEM images of deposit samples near the gas side of the deposit (left) and near the base of the deposit (right). Particles become less distinct the longer that they have been in the deposit.

Based on this body of data, REI developed a hypothesis to describe the mechanism whereby the deposits form on the syngas cooler surfaces. The mechanism proceeds in the following steps:

1. Metallic element release:
    - Some metals in the fuel are released/vaporized during gasification process;
2. Fume formation:
    - Vapor condenses into a sub-micron fume of pure metals, metal sulfides, and metal oxides;
    - The melting point of these species may be near or lower than temperatures typical of an IGCC syngas cooler; and
    - Gasifiers have a long residence time that promotes growth of fume particle size.
3. Initial deposition:
    - Submicron particulate and small ash particles deposit onto stagnation points in syngas cooler region; and
    - Forces important for small particles hold material in place (i.e., electrostatic and van der Waals). Thermophoresis is small since deposit is forming on an adiabatic surface.
4. Buildup and sintering:
    - Particles diffuse & sinter to form amorphous deposits with high structural strength;
    - There is some evidence of char particles depositing; and
    - Deposition mechanism doesn’t change as the deposit grows.

Based on the findings from the BP1 and BP2 research, REI concluded that using a sorbent to capture vaporized metals in the syngas would be an effective method to mitigate the SC fouling.

Task 3.0 – UofU Laboratory Scale Experiments

Objective: Perform laboratory scale experiments.

Deposit Strength Tests

Under this Task the UofU performed laboratory scale experiments to generate ash deposits on metal plates and determine the bond strength between the deposit and the plate. The testing utilized the UofU Laminar Entrained Flow Reactor (LEFR) and the 1 ton per day (tpd) high-pressure, pilot scale gasifier. The UofU was lead and responsible for all aspects of this Task.

The LEFR is a drop-tube reactor that can operate at high temperatures under gasification or oxidizing conditions (see Figure 10). The test procedures and test design for the jet cleaning tests performed with the LEFR were based on techniques described in the literature that were originally developed for analyzing deposits in pulverized coal fired electric utility boilers [Walsh et al., 1990], [Walsh et al., 1994]. Micronized fuel or ash particles were converted through partial oxidation at 1400°C in the reactor, after which they flowed downwards towards a small, removable, horizontally-oriented plate (see Figure 11). Tests were performed for plate temperatures ranging from 550C to 820C.

Many different fuels, including coal, petroleum coke and coal/petcoke blends were investigated. The OEM partner provided the following materials from a commercial installation:

- Petroleum coke (uncalcined “green” material used in the commercial plant)
- Fluxing agent that is mixed with the petroleum coke
- “As-fired” mixture of petroleum coke and fluxing agent (petcoke + fluxant)
- Material (char) removed from the syngas stream of the commercial plant

In addition, fine particulate material similar to that in syngas streams of commercial systems was generated by operating the UofU 1 ton per day, pressurized, pilot-scale gasifier with a range of fuels. The particulate matter was filtered from the syngas and collected. The adhesive bond strength between the impact plant and these materials was subsequently determined using the jet cleaning test in the LEFR system.

The strength of the bond between plate and deposit was determined by increasing the velocity of a small nitrogen jet aimed at the center of the plate (see Figure 12) and noting the velocity at which the deposit was cleaned from the plate. Videos of some of the jet cleaning tests were recorded using a cell phone camera to allow studying the failure process for the deposit. In general, two different deposit failure mechanisms were observed. For some tests, the entire deposit was suddenly lifted off the impact plate all at once leaving a relatively clean surface, indicating that the failure had occurred at the base of the deposit and that the shear stress caused by the jet had overcome the adhesive strength of the deposit. In other tests, pieces of the deposit broke off first around the jet stagnation point on the deposit, suggesting a failure stress was reached within the deposit at the jet stagnation point and that the tensile strength of the deposit was the source of the failure.

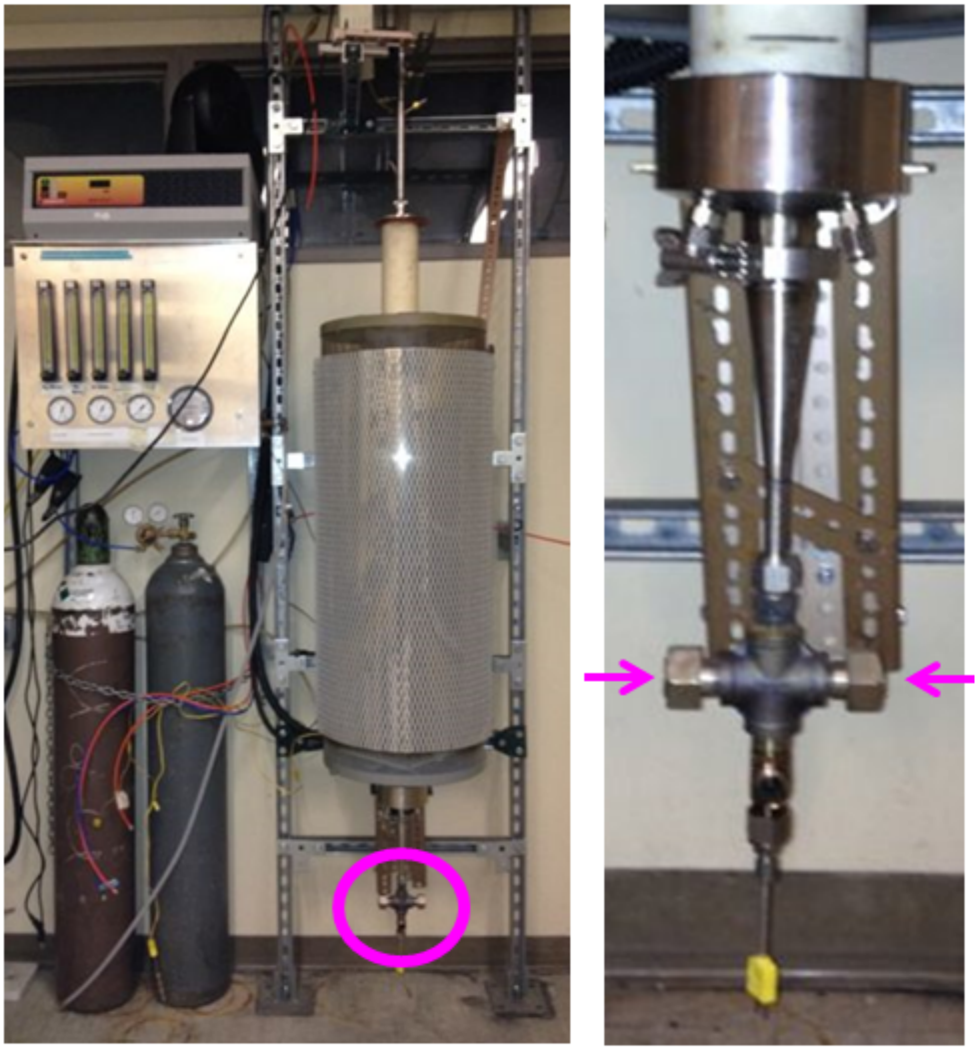


Figure 10. Photographs of LEFR Reactor. Full reactor (left) and with exit region highlighted and close-up view of LEFR exhaust region (right).

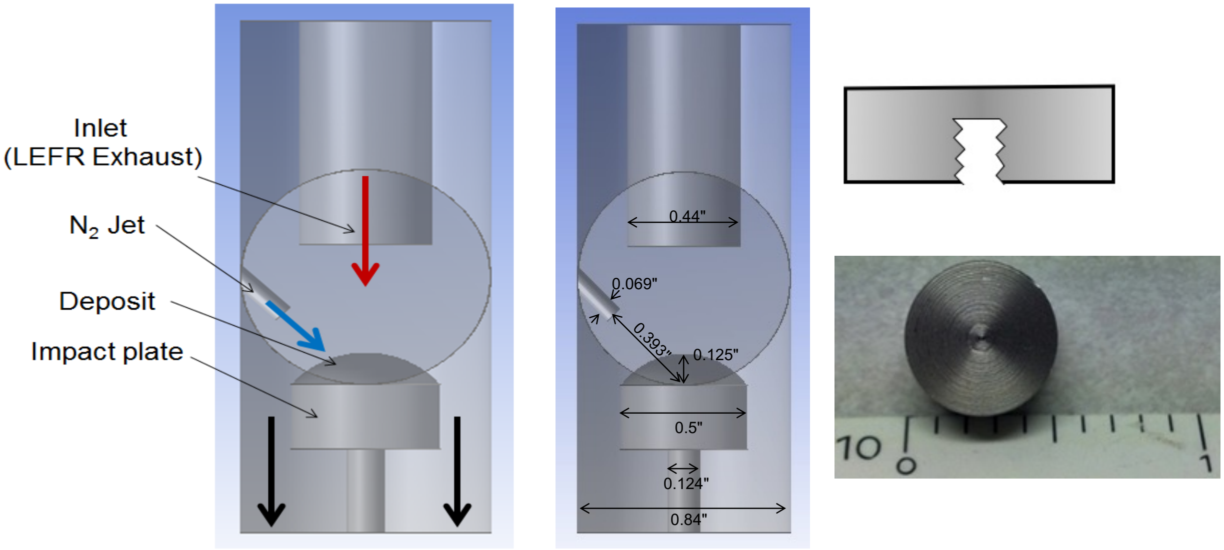


Figure 11. LEFR Exhaust Region Schematic. Image shows orientation of deposit plate and nitrogen jet (left and middle) and example impact plates (right top, right bottom).

Altogether over 230 jet cleaning tests were performed in the LEFR using different feedstock and test conditions. Results showed that the required jet velocity ranged between 20-90 m/s. Data for the fluxant, petcoke with fluxant mixture, char material, and green petcoke are shown in Figure 12. Major findings include:

- The data was consistent and repeatable.
- Deposit strength increases with the initial impact plate temperature in a linear trend. Increased plate temperature increases the rate of particle sintering that would occur, leading to stronger deposits. Cooling the SC tube sheet face may be a possible deposit mitigation strategy for future IGCC plants.
- Deposit strength increases rapidly with time. When deposits were left to sit on the plates before the jet was applied the strength of the deposits increased exponentially for the first few hours and then leveled off for longer time periods. This indicates that if sootblowing or another removal technology is employed it would be beneficial to remove the deposits frequently before they have built up strength.
- Ash material and coal produced the weakest deposits while char material and green petcoke from the plant produced the strongest deposits. The strength of deposits derived from petcoke with fluxant was close to the green petcoke, but the presence of fluxant material in the deposits appears to weaken the bond strength.
- Plate material (stainless vs. carbon steel) had little impact on the bond strength between the deposits and the plates. However, carbon steel plate did show greatly increased wear after only three uses. Stainless steel plates were much more durable.

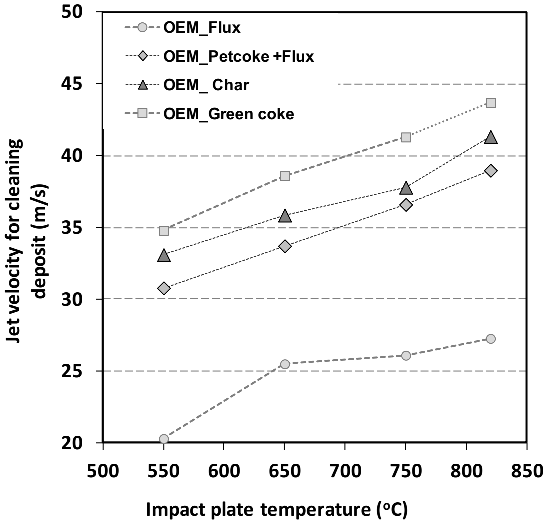


Figure 12. Jet velocity for cleaning the deposit at different deposition plate temperatures. Example result. Ex-situ tests. Samples: OEM_petcoke+flux and OEM_green coke samples gasified in LEFR. OEM_char and OEM_fluxant samples heated in N_2 environment. Plate: 304 stainless steel.

Sorbent Effectiveness Tests

Analysis of the deposit sample composition and particle size distribution data indicated that a very large portion of the deposits are made up of sub-micron particles that are enriched in vanadium and metal sulfides. A review of the literature indicated that kaolinite based sorbents had been successfully used to capture vanadium and other metals in the combustion of residual fuel oil. Experimental data on the ability of such a sorbent to capture metals in a gasification environment was needed.

Pilot-scale experiments to test the effectiveness of the sorbent at capturing vaporized metals in syngas were designed and conducted early in 2014 (i.e., BP2 – Q6 in Figure 2). The experiments were carried out in the oxy-fuel combustor (OFC), a 100 kW downward-fired, pilot-scale reactor (see Figure 13) located at the Industrial Combustion and Gasification Research Facility located at the University of Utah (UofU). The reactor can be oxy-fired using dry fuels and/or natural gas. The reactor consists of a vertical radiative section and a horizontal convective section and each section has several ports available for sampling. The reactor has previously been used in aerosol formation studies and is equipped with particle sizing instrumentation, making this reactor uniquely suited for these experiments.

Both coal and petcoke were used as a fuel with about 20% natural gas co-fed to maintain reactor temperature in the desired range. Pure oxygen was used as the oxidant. Oxygen/fuel ratio was adjusted to produce both oxidizing and reducing conditions for each fuel. Sorbent was co-fed with the pulverized fuel at feed rates ranging from 0 to 8 times (0, 2X, 4X, 8X) the *molar feed rate* of metals in the fuel ash. This corresponds to a sorbent feed rate of about 0 – 2.4wt% of the fuel feed rate.

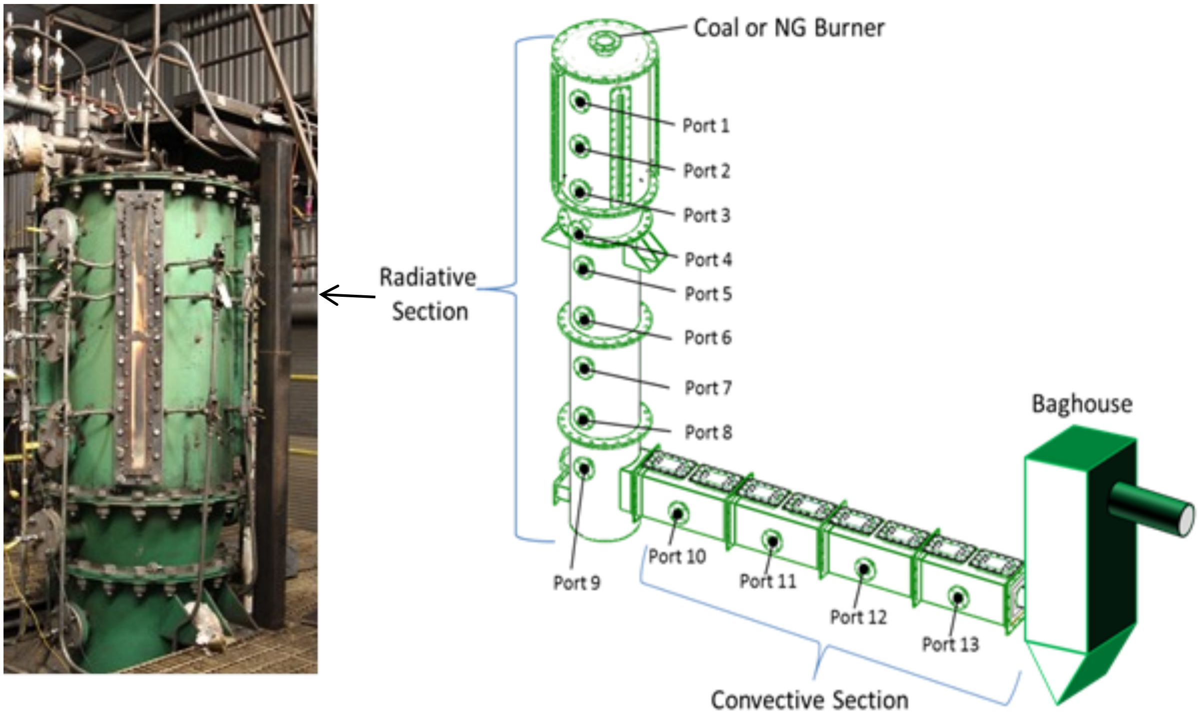
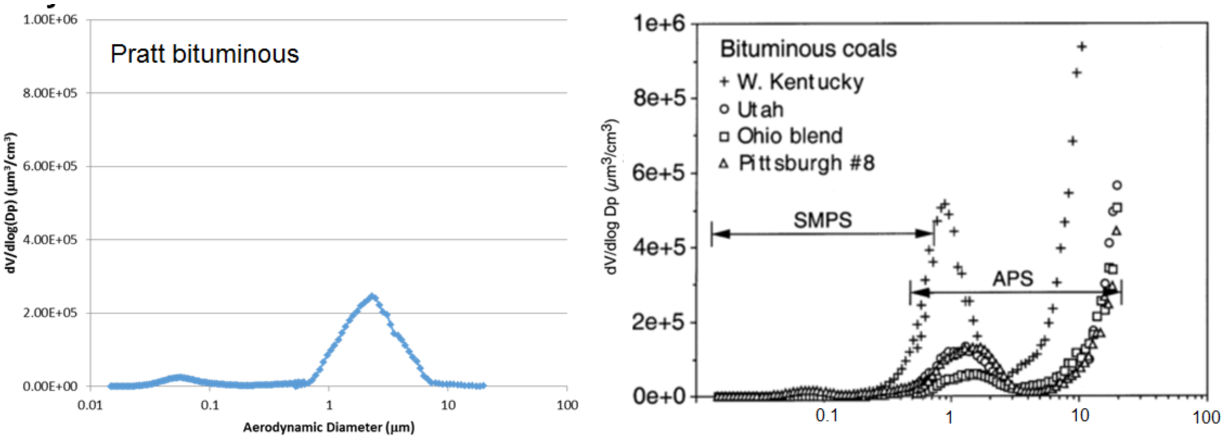


Figure 13. Photograph (left) and schematic (right) of the pilot-scale reactor used for the sorbent effectiveness experiments.

Gas temperature was measured at several points down the reactor and particle size distribution data were collected by inserting a measurement probe into Ports 5 and 8. To collect the deposit sample, an uncooled deposition probe (diameter = 1.50 in.) was inserted into Port 7. A 1.90 inch diameter tube was inserted into the port above to act as a shield to catch any large ash particles. The probe was allowed to stay in place for four hours to collect deposit material, after which it was carefully removed and the deposit was collected and measured. The data collected in this test was used to validate he amount of deposition predicted by the CFD model (see Task 4.0).

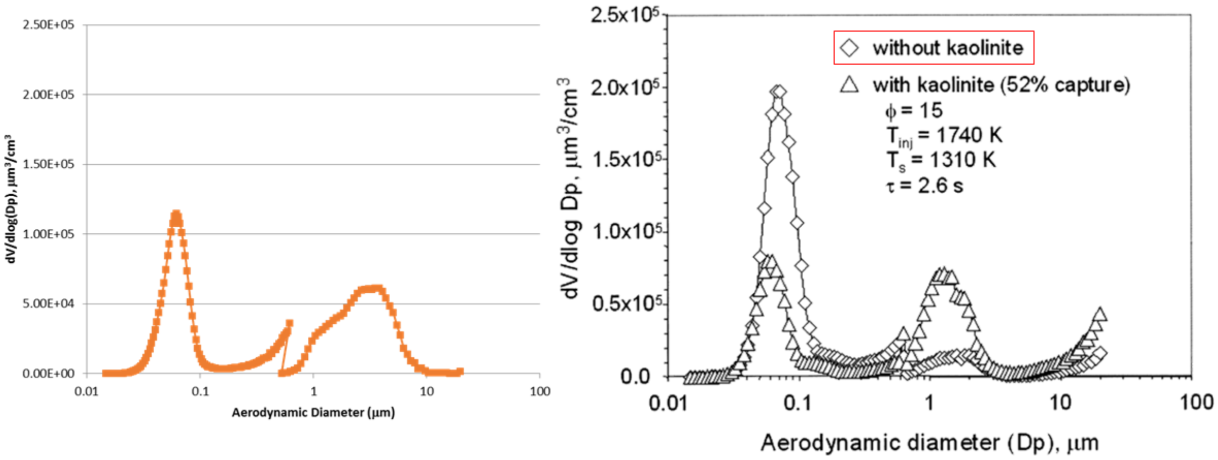
Gas-entrained particle measurement was performed using a combination of a scanning mobility particle sizer (SMPS) with an effective range of 14-615 nm (i.e., < 1 µm) and an aerodynamic particle sizer (APS) with a particle size range of 0.5 µm to 19 µm. Particle size distributions were compared to those found in the literature [Linak, Miller, & Seames, 2002] and shown in Figure 14 and Figure 15 and found to have good agreement.



REI 2014

Linak et al. 2002

Figure 14. Particle size distribution data for bituminous coal from the UofU entrained flow reactor experiments performed in this project (left) and work performed by Linak et al., 2002 (right).



REI 2014 – Petcoke without sorbent

Linak et al. 2004 – Residual Fuel Oil

Figure 15. Particle size distribution data for petcoke with fluxant from the UofU entrained flow reactor experiments performed in this project (left) and work performed by Linak et al., 2004 using residual fuel oil (right).

The particle size distributions when sorbent was used were compared to the data obtained during baseline runs (i.e., no sorbent). For all of the tested sorbent addition rates a very large reduction in particles was observed (see Figure 16). Submicron particulate was reduced by >90% on a mass basis. Particles in the range of 1-19 µm were reduced by about 50% on a mass basis.

- ***This data indicates that even a small amount of sorbent (i.e., dosage = 0.6wt% of the fuel = 2X wt% of the ash in the fuel) greatly reduces the amount of fine particulate in the syngas that contributes to the formation of SC deposits and thus may be a very effective mitigation strategy.***
- Similar results were obtained for using a sorbent dosage = 2X, 4X and 8X wt% of the ash in the fuel, indicating that a lower sorbent dosage could potentially provide similar rates of metal capture. Additional testing would be required to determine the lower limit for sorbent dosage concentration that provides good metals capture.

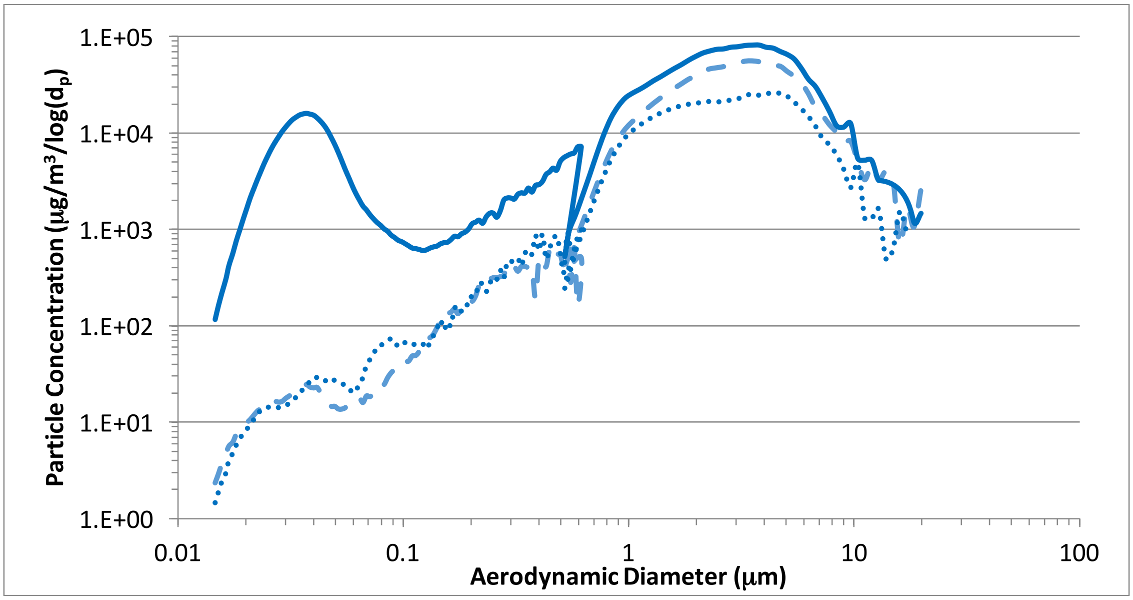
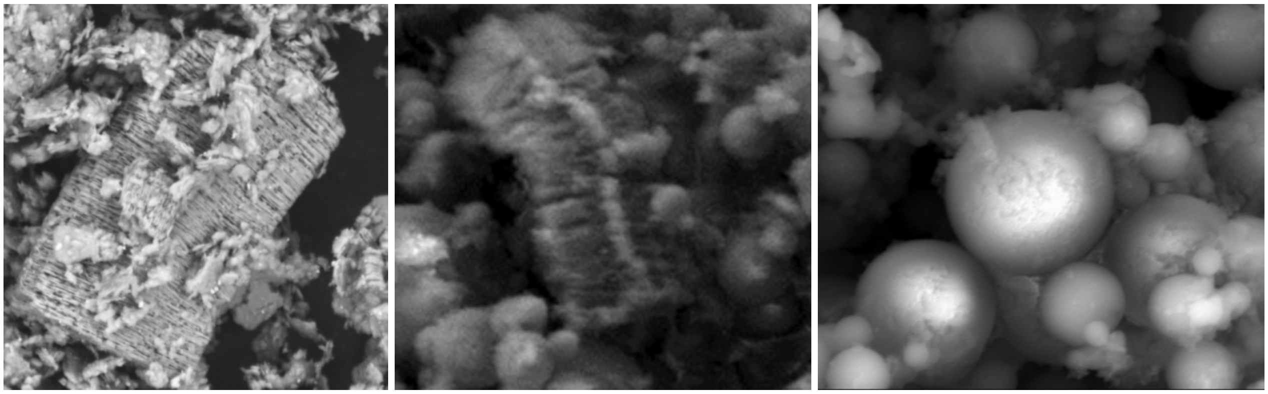


Figure 16. Particle size distribution comparing baseline results with no sorbent addition (solid line) and results for sorbent additions (dashed and dotted lines) shows > 90% reduction in mass of particulate less than 1 µm in size and 50% reduction in mass of particulate in the 1-20 µm size range.

Figure 17 illustrates the changes in the sorbent during the adsorption process [Linak et al., 2004]. Initially the raw sorbent is not activated. When the raw sorbent is heated to > 500C the sorbent "activates" and the surface area of the sorbent expands. Metals chemically react with the sorbent surface forming low temperature eutectics. These compounds melt in the high temperature environment, forming spheres and trapping the metal.



Un-activated sorbent

Activated sorbent

Melted Sorbent and Metals

Figure 17. Illustration of sorbent adsorption process. Shown are un-activated (raw) sorbent (left), activated sorbent (middle) after heating sorbent to > 500C and melted sorbent and metals (right).

In a practical application the sorbent material injected into the gasifier to capture vaporized metals will itself be captured in a downstream char filter and then re-cycled to the hot section of the gasifier where the re-cycled char and used sorbent is re-heated to about 1600C and presumably will exit the gasifier in the flowing slag that exits via the tap hole. Gasifiers use recycle loops to increase the carbon conversion of the fuel. A potential concern is that the fume captured by the sorbent might be released when the used sorbent is re-heated. To investigate this question a scoping study was performed in which used sorbent material was extracted from the OFC baghouse after performing a sorbent effectiveness test, re-heated in a Thermo-Gravimetric Analyzer (TGA) and the mass of material as the sample is heated was recorded. Samples were tested in three environments: air; 5%H2 + 95% N2; and 100% N2 (inert). The TGA results were similar for all three environments.

Illustrated in Figure 18 is an example result for the TGA test. Shown is the sample mass versus temperature. The sample mass changed very little during the test. There is less than 2% mass loss at 1050C and ~3 wt% loss at 1500C, indicating only a small amount of gas was released. The composition of the off-gas released during the TGA test was not determined. An improvement to this test would be to use a Mass Spectrometer (MS) to identify the composition of the off-gas released from the sample to determine if any of the captured metals are contained in the off-gas.

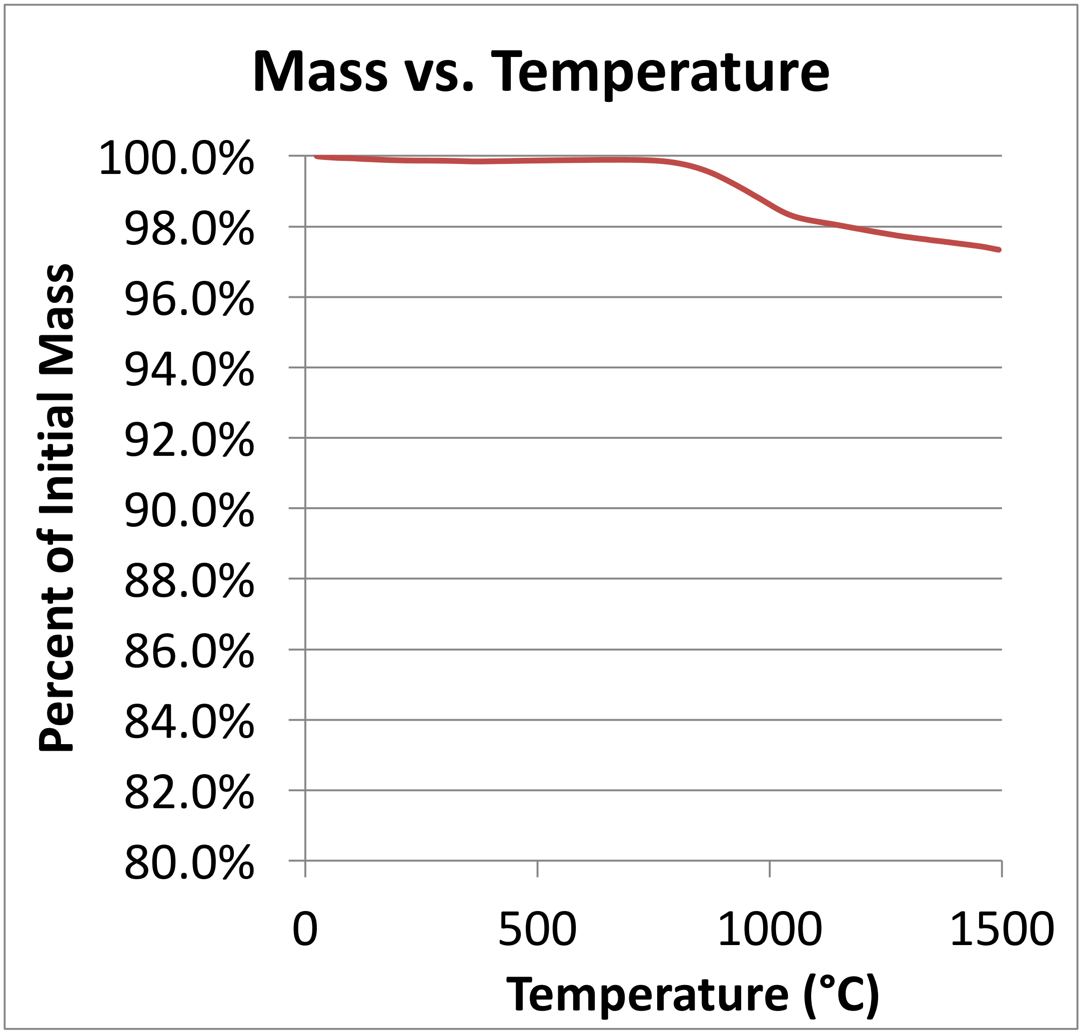
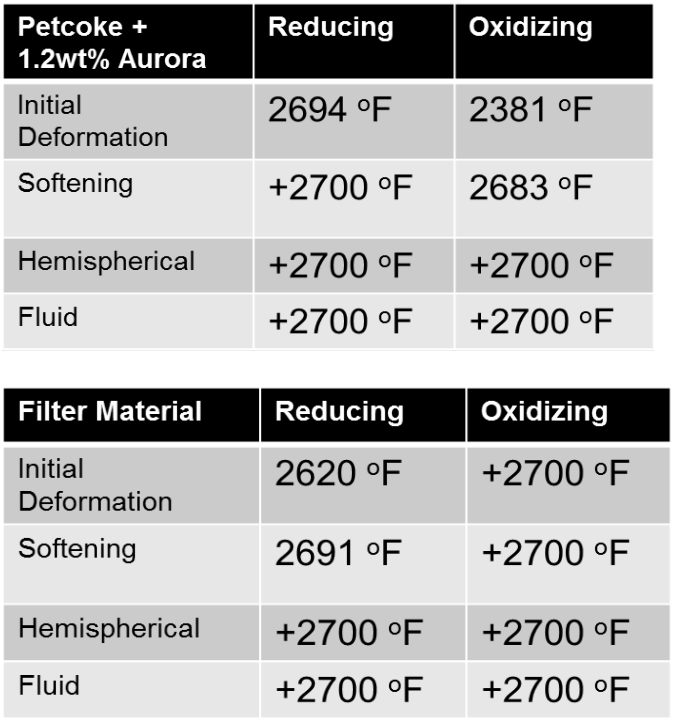


Figure 18. TGA analysis of re-heated OFC baghouse filter material (used sorbent and char) shows < 2% decline in mass at 1050C, gradual decline at higher temperatures. Overall less than 3% of the mass was removed from the sample by heating to 1500C.

An additional concern was the impact on the slag viscosity due to the used sorbent material being in the flowing slag in the hot section of the gasifier. The sorbent is primarily alumina-silicate and thus will tent to increase the viscosity of the slag.

A scoping study was performed to provide insight into this issue. Material (used sorbent and char) was collected from the OFC baghouse filters after the pilot-scale sorbent tests were completed. The collected material was heated to 800C in a muffle furnace to remove and moisture and carbon. The sample was estimated to be about 70wt% used sorbent and 30wt% ash. Ash fusion temperature tests were performed using the baghouse filter material and OEM-provided petcoke mixed with 1.2wt% Aurora^{TM} sorbent.

Ash Fusion Temperatures (AFT) were determined for Initial Deformation, Softening, Hemispherical and Fluid Temperature for oxidizing and reducing conditions for (a) Petcoke + 1.2wt% Aurora^{TM} sorbent mixture and (b) the OFC baghouse filter material. Note that 1.2wt% sorbent is ~4X wt% of the ash in the petcoke. Illustrated in Figure 19 are the test results. The test results indicate an AFT of nearly 2700F (1482C), indicating that additional fluxant would need to be added to the fuel mixture to ensure a flowing slag.



Petcoke + 1.2wt% Aurora	Reducing	Oxidizing
Initial Deformation	2694 °F	2381 °F
Softening	+2700 °F	2683 °F
Hemispherical	+2700 °F	+2700 °F
Fluid	+2700 °F	+2700 °F

Filter Material	Reducing	Oxidizing
Initial Deformation	2620 °F	+2700 °F
Softening	2691 °F	+2700 °F
Hemispherical	+2700 °F	+2700 °F
Fluid	+2700 °F	+2700 °F

Figure 19. AFT data for petcoke mixed with sorbent and OFC baghouse filter material (used sorbent and char).

Experiments To Collect Deposition Data To Validate CFD Deposition Model

Additional tests were performed in the OFC without sorbent injection to provide deposition data that could be used to validate the deposition build-up sub-model contained in the REI CFD model. Bituminous coal and petcoke were used as fuels. The fuels were fed into the reactor with pure oxygen under both oxidizing and reducing stoichiometries. Natural gas was added to the reactor to maintain the temperature profile in the reactor across the four cases.

The objective of the experiments was to provide high-quality deposition rate data for a range of syngas-cooler relevant conditions for use in validating the CFD deposition sub-model used in this project. To collect deposition rate data, an uncooled probe was inserted into the flow of product gases approximately 1.5 m from the end of the flame region. A deposit was allowed to build for four hours and then the probe was removed and the deposit sample was collected and measured.

All inlet parameters, including mass flow rates of gas and particles, gas temperatures and pressures were recorded. Particle size distribution for each case was determined using data recorded by the SMPS and APS. A discussion of the measured and predicted deposition values is provided in Task 4.0 – Modeling.

Task 4.0 – Modeling

Objective: *Perform process and CFD modeling to investigate deposition in the SC.*

In this Task REI has performed a range of modeling calculations to: support and interpret data from the UofU laboratory scale tests; CFD modeling to investigate fouling and plugging of the SC; and CFD modeling to evaluate potential design/process changes to mitigate fouling and plugging of the SC. The conditions and scenarios modeled were discussed and defined in internal project review meetings.

Using information in the open literature and engineering judgment, REI developed geometries representative of SC designs. The model consists of a transition duct, tube sheet face and a tube bank. Note that SCs use a firetube heat exchanger design. For modeling purposes the tube sheet face was assumed flat. At the entrance to each tube the flow area was tapered for a short axial distance to reduce erosion and deposition that could occur at the tube inlet if an abrupt flow area transition were used. In some commercial designs a ferrule is used at the tube entrance. The ferrule is an insert that couples the tube to the tube sheet. The ferrule has an engineered design to provide a smooth flow transition. The ferrule can provide a "sacrificial" insert that can be replaced if excessive wear and/or fouling has occurred. After the transition region the tubes have a constant diameter. The tubes are assumed to be twenty (constant) tube diameters in length. The surface temperatures of the tube walls and tube sheet surface are determined via a wall model boundary condition used by REI for modeling heat exchangers that employ backside cooling.

Deposition in the SC was predicted using the REI fouling and deposit buildup model. It is a mechanistic model that includes the impacts of

- ash properties (e.g.local particle composition, particle size, temperature, density, viscosity, surface tension),
- included/excluded minerals (e.g., pyrite),
- local conditions (gas composition, temperature, heat flux to surfaces)
- properties of deposits (composition, temperature, density, viscosity, surface tension (if wet), strength of sintered material).

The model provides predictions for the properties of particles exiting the furnace in-flight, deposition rate (growth rate) and properties of the sintered deposits on walls, and the impacts of fouling on gas phase properties, overall heat transfer, etc. The model builds on the work of many investigators, including [Walsh et al., 1990, 1992], [Wall et al., 1979, 1993], [Gallagher et al., 1990, 1996], [Senior and Srinivaschar, 1995], [Wang et al., 1997, 1999]. A schematic of the model is shown in Figure 20.

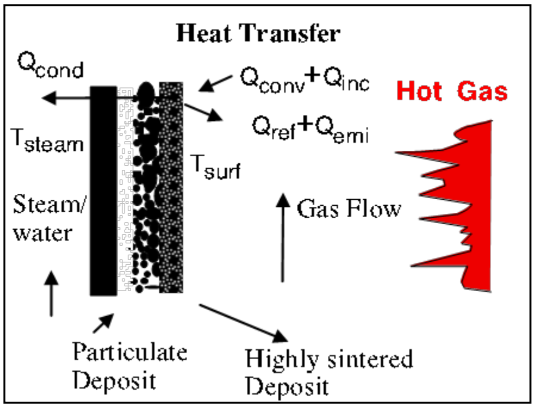


Figure 20. Schematic-REI fouling and deposit buildup model.

During the course of the project several enhancements to the Fouling and Deposit Buildup Model were implemented. In particular the particle cloud model was replaced with a stochastic particle tracking model to better capture the "randomness" due to turbulent effects on particle trajectories. A grid deformation algorithm was implemented to better represent the buildup of deposited material on surfaces. Also implemented was a more general criteria for particles sticking to surfaces in the SC.

The fouling and deposit buildup is implemented into REI's in-house comprehensive, reacting Computational Fluid Dynamics (CFD) code for use on commercial and research projects. The CFD model provides all needed information about local conditions and the output of the fouling model is coupled to calculations for overall mass, momentum, energy, speciation, etc. The fouling model can also be used in a "standalone" mode, but requires specifying the local conditions for the hot gas. The model provides more accurate predictions of fouling impacts than could be performed previously and has proven particularly useful for investigating the impacts of fuel switching and changing firing conditions on boiler performance Further details on the REI fouling model are available in [Adams et al., 2009]. However, it should be noted that traditional approaches for estimating sticking temperatures have relied upon empirical relationships related to ash fusion temperatures. Our literature research, modeling calculations and analysis of the fouling deposits from commercial IGCC equipment have led us to refine our hypothesis for deposit growth in the SC. These refinements have been made in recognition of a deposition mechanism that can result in initiation at temperatures well below ash fusion temperatures.

Validation of CFD Model Predicted Deposition

Tests were performed in the OFC without sorbent injection to collect deposition data that could be used to validate the deposition build-up sub-model contained in the REI CFD model. Bituminous coal and petcoke were used as fuels. The fuels were fed into the reactor with pure oxygen under both oxidizing and reducing stoichiometries. Natural gas was added to the reactor to maintain the temperature profile in the reactor across the four cases. The objective of the experiments was to provide high-quality deposition rate data for a range of syngas-cooler relevant conditions for use in validating the CFD deposition submodel used in this project. To collect deposition rate data, an uncooled probe was inserted into the flow of product gases approximately 1.5 m from the end of the flame region. A deposit was allowed to build for four hours and then the probe was removed and the deposit sample was collected and measured.

The geometry of the OFC was replicated for the CFD model with the model geometry beginning at Port 3 and extending down to Port 8 (see Figure 21). A CFD case for each of the experimental conditions (coal or petcoke in oxidizing or reducing conditions) was run. All inlet parameters, including mass flow rates of gas and particles, gas temperatures and pressures were derived from experimental values. The Particle size distribution (PSD) used for each case was based on SMPS and APS data from the OFC experiments performed to provide the model validation data.

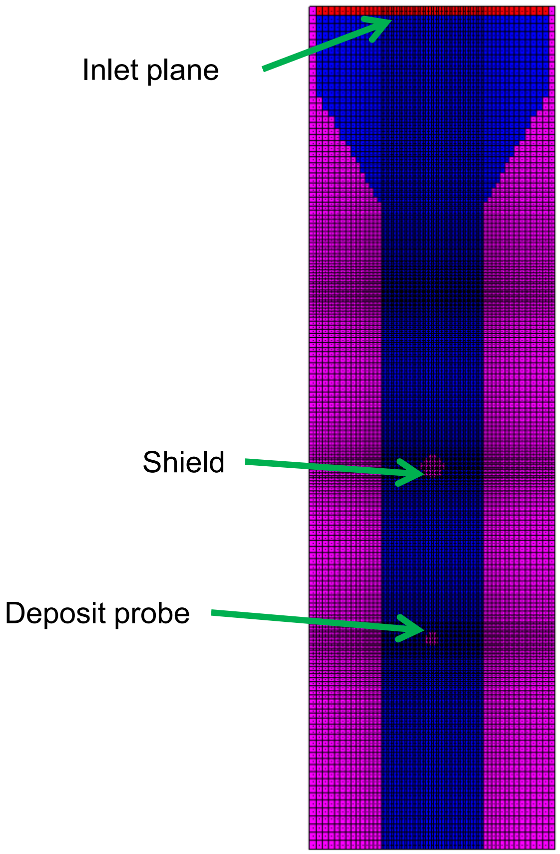


Figure 21. 2D slice of 3D CFD model of OFC reactor used for deposition sub-model validation.

Illustrated in Figure 22 is a comparison of the predicted and measured deposition rates. Overall, there is good agreement between the predicted and measured values. These results gave REI confidence in the deposition sub-model. Based on these results REI considered the deposition sub-model to be sufficiently validated and Milestone #10 completed. This satisfied Action Item AES-1 from our AES review.

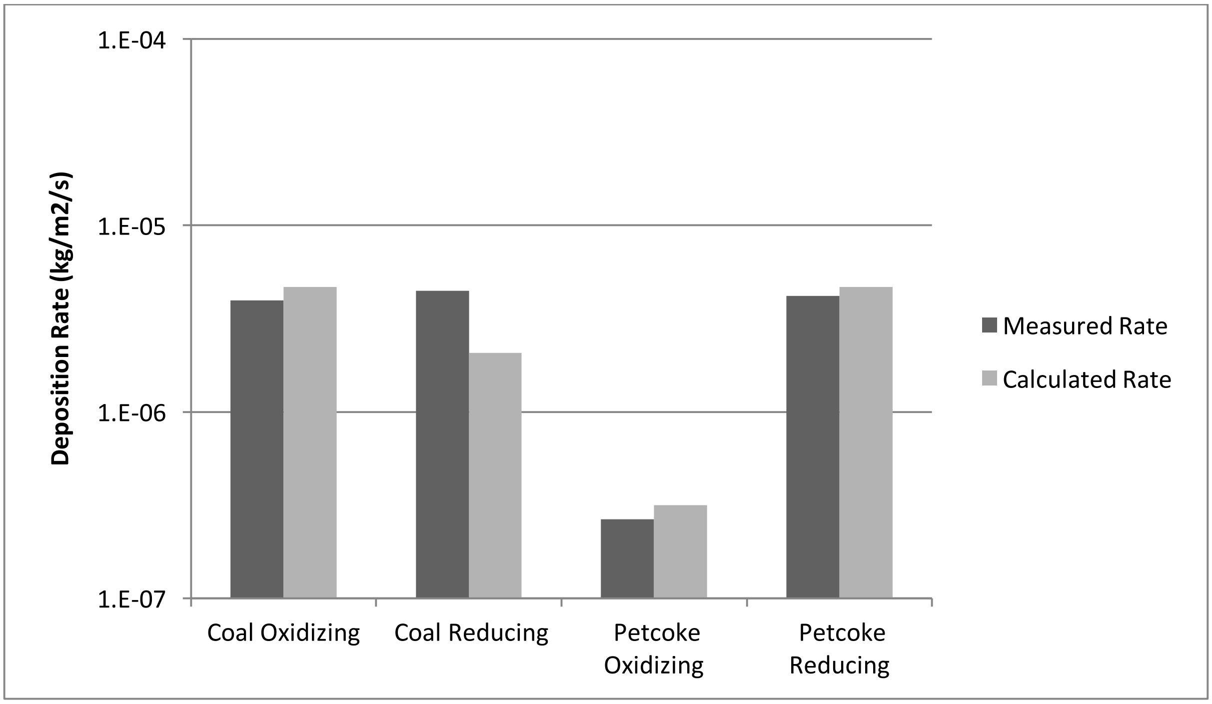


Figure 22. Validation of deposition sub-model.

CFD Modeling to Determine Deposit Strength

CFD modeling was performed to support experiments performed in the Laminar Entrained Flow Reactor (LEFR), a drop tube reactor, at the University of Utah. Deposits were formed on the plate using coal, green petcoke (petcoke without any additives), petcoke with fluxant added, and samples of deposits found in IGCC syngas cooler systems. The plates with the deposits were allowed to cook in a muffle furnace at 650C for 1hr, 24 hrs, or 1 week. Afterwards, the plates were placed into the exhaust section of the LEFR and a nitrogen jet was aimed at the center of the plates (Figure 23) was used to exert pressure on the deposit. The velocity of the jet was increased until the deposit failed, and the velocity of the jet at which the deposit failed was recorded. Experimental values for the jet cleaning velocity ranged from 15-85 m/s.

Videos were taken of the removal process performed in a different experimental apparatus for the purpose of video recording. Similar deposits plates were subjected to the same velocity jet nozzle. The videos show two different deposit failure mechanisms. In one video, the entire deposit was suddenly lifted off at once leaving a relatively clean surface, indicating that the failure had occurred at the base of the deposit and that the shear stress caused by the jet had overcome the adhesive strength of the deposit. In another video, pieces of the deposit broke off first around the jet stagnation point on the deposit. This suggests a failure stress was reached at the jet stagnation point; that the tensile strength of the deposit was the source of the failure.

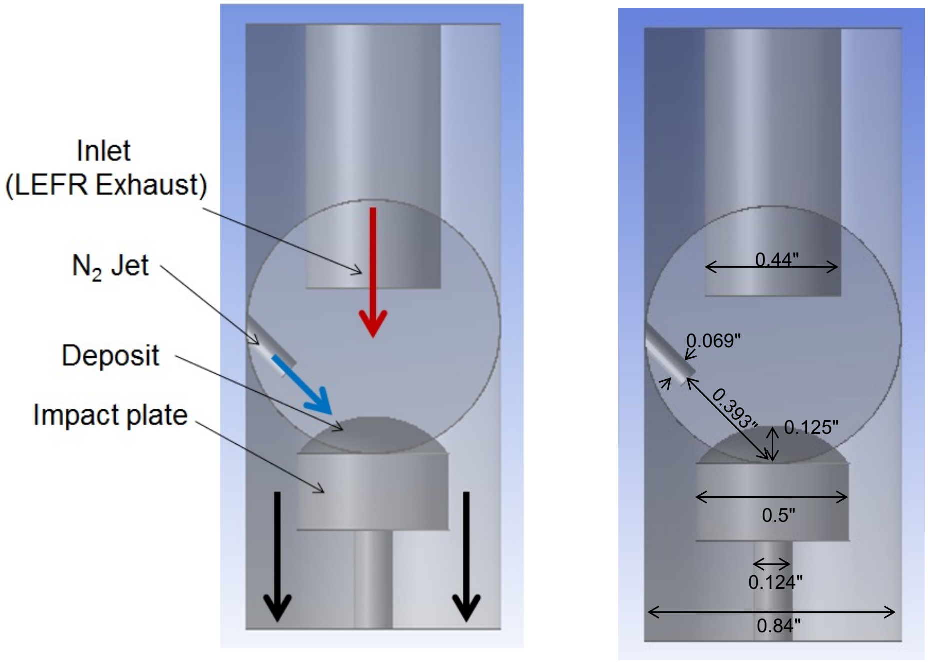


Figure 23. LEFR exhaust region showing orientation of deposit plate and nitrogen jet.

The purpose of the CFD modeling was to estimate the actual deposit strength (both adhesive and tensile strength) from the recorded jet velocity where the deposit was removed. For this analysis a representative jet velocity of 25 m/s was used. From conservation of momentum, the strength of the deposits removed at other jet velocities can be estimated by multiplying by the square of the velocity ratio.

$$strength = strenth_{25\ m/s} \left(\frac{v}{25\ m/s} \right)^2$$

The operating conditions for the CFD model are given in Table 4. ANSYS Fluent 14.1 was used for the CFD modeling. Figure 24 shows the predicted gas velocity and temperature distributions. Figure 25 shows the total (stagnation) pressure including the jet axial profile of the total pressure.

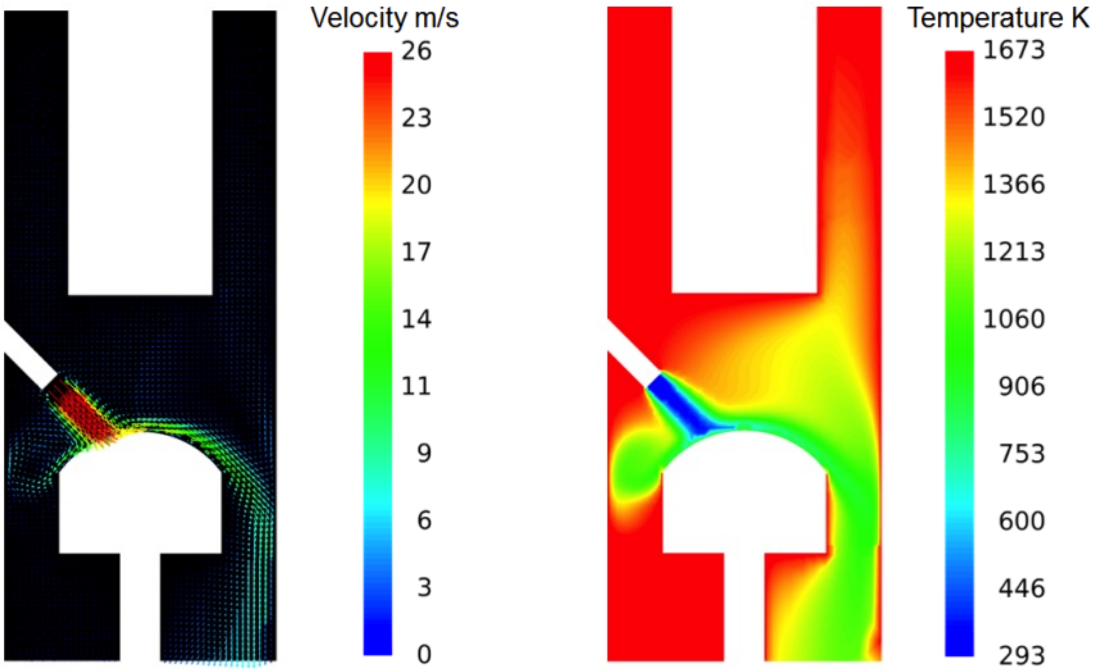


Figure 24. Predicted gas velocity and gas temperature distributions.

Two different strength parameters were derived from the CFD results: 1) The average shear stress at the base of the deposit and 2) the peak total pressure at the stagnation point of the jet on the deposit surface. To determine the mean shear stress at the base of the deposit, the total force in the shear direction was extracted from Fluent. The resulting shear strength is then simply this force divided by the area of the plate. Table 5 provides the resulting average stress. The results indicate that the adhesive strength of the deposit is very weak.

Table 4. LEFR Operating Conditions

LEFR Exhaust Temperature C	1400
Ambient Pressure, kPa	85.6
Deposit and impact plate temperature, C	650
N_2 Jet temperature, C	20
N_2 Jet velocity, m/s	25
Inlet mass flow rate, kg/s	0.00525

Table 5. Derived average shear strength for a removal jet velocity of 25 m/s.

Shear component of pressure force, N	0.000473
Shear component of viscous force, N	0.000150
Total shear force, N	0.000624
Average shear strength, Pa	4.93

To estimate the tensile strength of the deposit, the pressure exerted by the jet onto the deposit was considered. The total pressure at the stagnation point created as the jet impacts the deposit is known as the peak impact pressure (PIP) and is a key parameter used to determine removal of a deposit [Kaliazine, et al., 1997, Eslamian, et al., 2008]. Kaliazinne, et al. [1997] have shown that the PIP needed to break the deposit is approximately twice the tensile strength. From Figure 3 the PIP for the 25 m/s condition would be about 240 Pa which corresponds to a tensile strength of 120 Pa. This is higher than that obtained from a Mohr's circle analysis based on the average shear strength at the base of the deposit. The results agree with similar analysis performed by Dockter et al. [1996] which found coal ash deposits have a tensile strength of 25-240 Pa.

- Developing an estimate of the adhesion bond strength between deposits and the surface to which the deposit is attached satisfied Action Item AES-3 from our AES review.

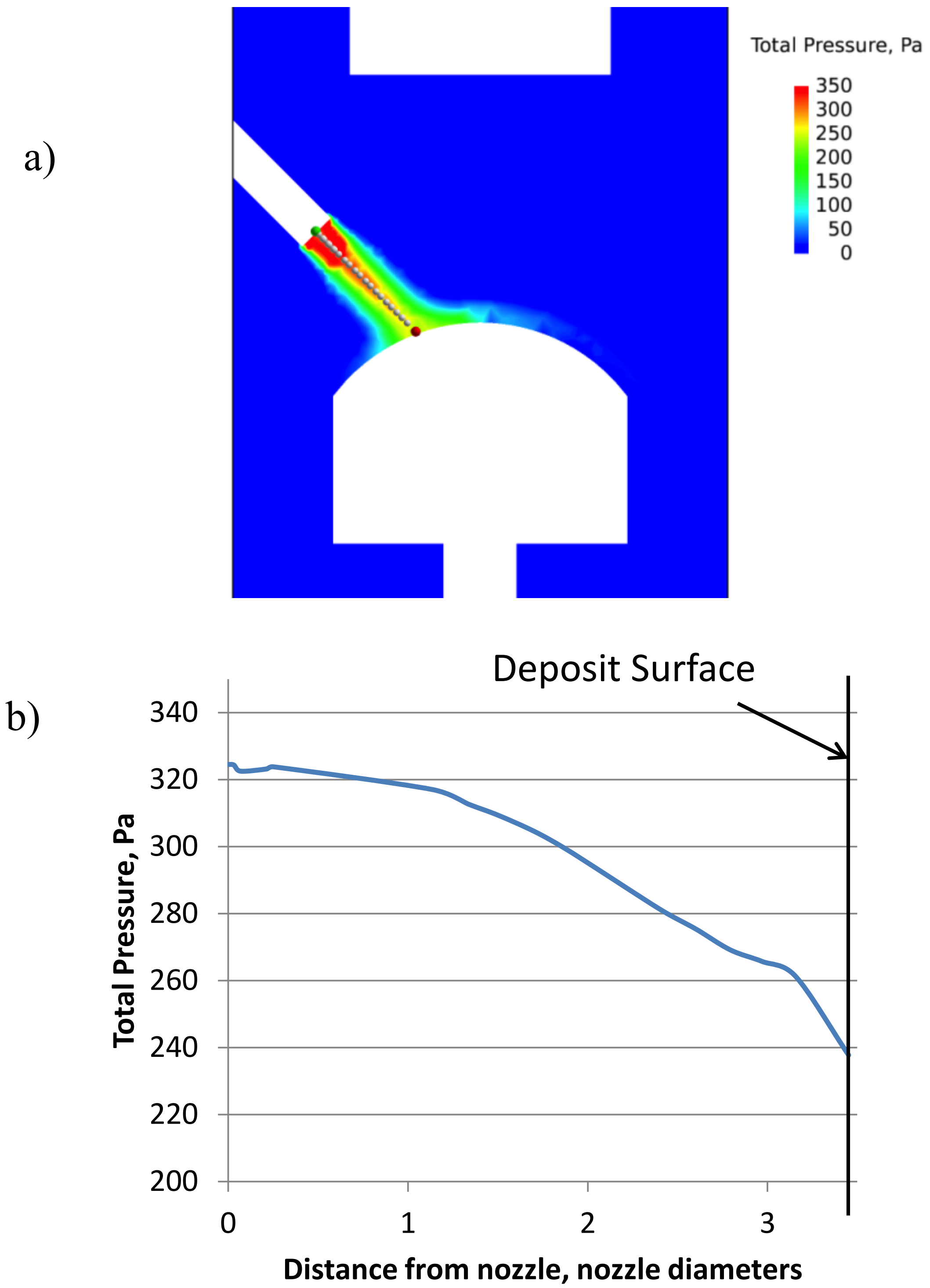


Figure 25. a) The total pressure distribution including the jet axial path. b) The total pressure profile along the jet axial path.

CFD Modeling of SC Geometries

REI performed a parametric study using in-house modeling tools. The CFD tool included a deposit formation submodel that allows the geometry to adapt while the model runs, simulating the growth of deposits on flow surfaces. Initially SC geometries were modeled. However, it quickly became apparent that the needed information could be obtained by modeling just a 3x3 tube layout subsection of the SC. Hence, to reduce computational time to perform the modeling study we focused on evaluating only a 3x3 section of tubes. Tube inside diameters of 1.0”, 1.5”, and 2.0” were modeled. The selected tube IDs span the range of tube sizes typically used in syngas coolers; older syngas cooler designs tended to use smaller (< 1.5”) ID tubes.

Illustrated in Figure 26 are representative modeling results. The surfaces in the figure are colored according the relative deposition rate on that cell surface with red indicating high amounts of deposition and blue indicating little or no deposition. Note that the deposition is concentrated around the tube inlets and that virtually no deposition occurs in the tubes. This trend is in agreement with field observations. For each scenario, the geometry was modified so that the cross-sectional flow area of the model domain was constant across the different cases. The parameters involved in the study included varying numerical parameters contained in the model, syngas conditions (particulate flow-rate and particulate size/spatial distribution), syngas cooler geometry (tube ID, tube inlet size/shapes) and upflow versus downflow SC orientation. In all, 46 models were produced and evaluated.

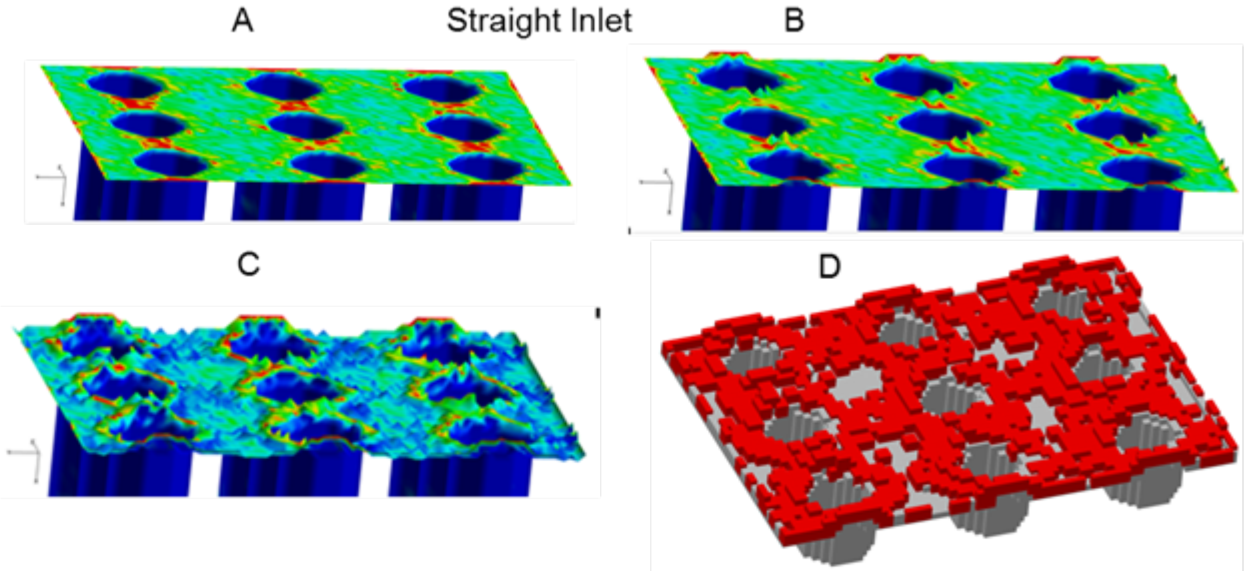


Figure 26. CFD modeling with deposit growth results. Initial deposition before grid changes (A), after a short time of deposit growth (B) and after a long period of growth (C). Image (D) shows the grid cells that have been changed as the deposits have grown.

Findings from the parametric study include the following.

- Increasing the diameter of the tube leads to lower deposition rates with a tradeoff of lower heat transfer efficiency. Figure 27 summarizes the modeling results for the three tube IDs evaluated. Shown in the figure is the predicted amount of deposition scaled by different geometric parameters..

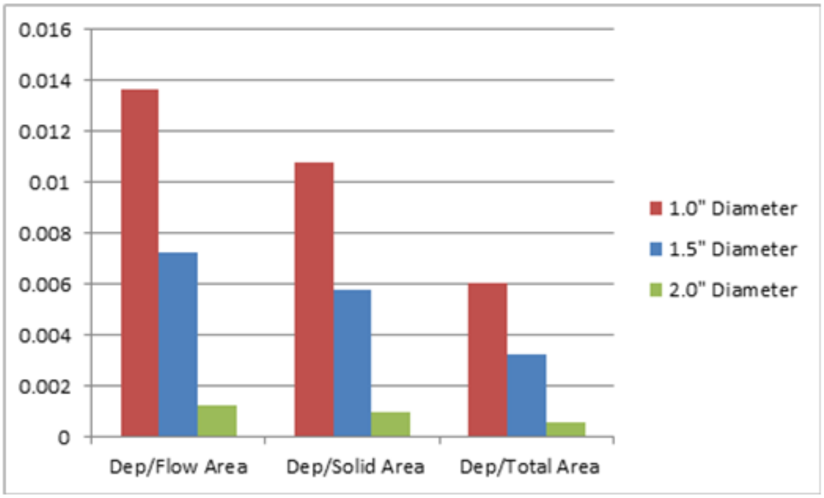


Figure 27. Amount of deposition vs. tube diameter.

- A funneled tube inlet provided a smoother flow transition but also provide a shape that can collect large pieces of deposits that originated upstream (e.g., chunk of deposit that spalls off during a thermal cycling event). Normal, flat tube inlets where the tube end meets the tube sheet face at a 90 degree angle and funneled inlets where the tube gradually narrows as the flow enters the tube were evaluated. Historically, syngas cooler designs have used both configurations. The funneled inlets greatly reduced the amount of deposition on the tube sheet face.
- A SC with the tubes arranged in a a staggered ("packed") rather than orthogonal pattern resulted in somewhat lower amounts of deposition, possibly due to their being less surface area on which deposits could form. In addition, the staggered pattern also allows for using more tubes within a prescribed syngas cooler vessel ID (i.e., tighter tube packing), potentially increasing the heat extraction from the syngas (see Figure 28).

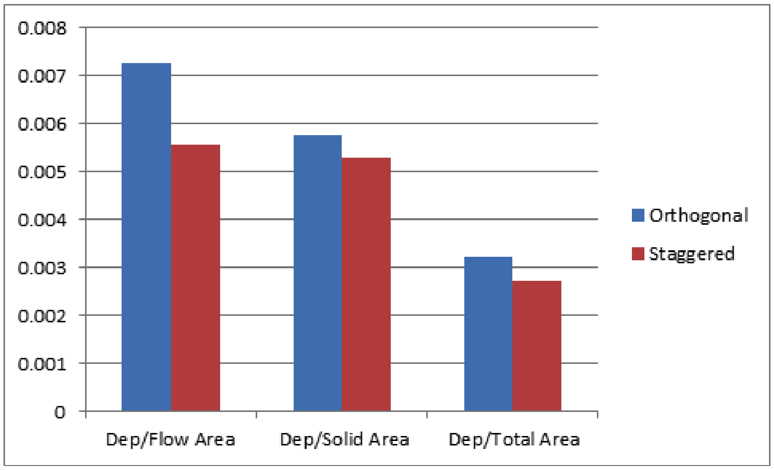


Figure 28. Comparison of the orthogonal and staggered tube arrangement results. Staggered tube arrangements produced slightly lower deposition rates than the orthogonal tubes.

- Modeling results for reducing the temperature of the tube sheet face to match the temperature of the tube walls were inconclusive. Current practice is for the tubesheet face to be insulated and thus at about the same temperature as the syngas. One hypothesis is that operating the tubesheet face at a significantly reduced temperature will change the temperatures of the local syngas field and particulate impacting the surface, causing the particles to not stick to the surface and thereby reducing particle deposition. The modeling results showed no benefit (i.e., no reduction in deposition).
- Small geometry changes in the syngas cooler are unlikely to have a significant impact on the rate of deposition.

Overall, the CFD modeling indicates that the key focus points for eliminating SC deposits are reducing the amount of submicron particulate entrained in the gas phase and/or implementing drastic geometry changes to reduce stagnation planes in the flow field.

Process Modeling – Sorbent Injection Strategies

Laboratory data demonstrate that sorbents and limestone can be used to capture (remove) from the syngas vaporized inorganic species that lead to fouling deposits (i.e., metal sulfides, vanadium, sodium).

Thermodynamic modeling was used to scope the effectiveness of two sorbents, kaolinite and limestone, for capturing these species. HSC [39] was used to perform the calculations. The assumed composition and flow rate of Syngas and the assumed amount of inorganic fine particulate in the syngas for these calculations were based on fuel analysis and deposit sample analysis. Sorbent material was added to the system in various concentrations.

Modeling results demonstrated that both sorbents are effective for removing sulfides and vanadium species from the syngas.

- Limestone is well suited for capturing sulfur and was more effective for injection into a hotter, upstream environment.
- Kaolinite is well suited for capturing sodium and vanadium. Due to the propensity of kaolinite to form low-melting eutectics when combined with several metal elements, the sorbent was calculated to be more effective for downstream injection.

Capture efficiency in excess of 60% is predicted for a sorbent feed that is 3% of the fuel feed rate. However, there is a diminishing return to the benefit as the sorbent co-feed rate approaches the 3% value. Based on the literature and discussions with industry, in practice the sorbent injection is usually limited to 2% of fuel feed rate.

The modeling based evaluations noted above were completed approximately one year before the sorbent effectiveness experiments in Task 3 were performed at the UofU. The technical evaluations (calculations) for using Limestone and Kaolinite as additives were performed in BP1–Q4 and BP2–Q1, respectively, and the economic evaluation for using these additives was performed in BP2–Q2.

Task 5.0 - Economic evaluation and impact on COE of SC improvements

Objective: Perform Techno-Economic Analysis for COE due to improved performance of SC

A techno-economic analysis was performed to judge the economic feasibility of the proposed mitigation strategies. For the initial analysis, the economic impacts of employing sootblower technology or using a sorbent to control deposits in the SC was compared to baseline data. A more in-depth analysis was later performed to understand the economic implications of sorbent use.

To protect the plant's confidentiality, the analysis was based on plant operation cost data from publicly available technical reports [Wabash River Energy Ltd., 2000]. Costs for mitigation strategies were based on cost data obtained from relevant suppliers and economic data was used to calculate a representative cost of electricity (COE), a common metric for power plant evaluation. Calculations were performed using the Lifetime Cycle Analysis Tool (LCAT), software developed by NETL and Sandia National Laboratory [DOE-LCAT, 2012]. The input data and results were reviewed by the OEM and IGCC plant personnel collaborating with this project and were deemed to be an accurate representation of the expected financial benefit of reducing or eliminating the deposit buildup.

Sensitivity analysis of operation and maintenance, fuel, and capital costs and plant availability showed that availability and capital costs are the controlling parameter with O&M and fuels costs having a much lower impact on overall COE (see Figure 29).

The initial analysis indicated that sorbent use had the potential to reduce the COE. From performance reports, the amount of plant downtime caused by SC fouling accounted for a large amount of the total plant downtime, equal to approximately 17% total loss in availability. It was estimated that sorbent use could increase plant availability by 4.3% resulting in a 2.8% reduction in COE.

A second analysis was performed to provide a more in-depth look at the economic feasibility of using a sorbent to mitigate SC deposit formation. Increased operating and maintenance costs associated with increased slag disposal and fluxant requirements were included in this calculation along with material and installation and maintenance costs for the equipment needed for sorbent injection. The COE was calculated for several sorbent addition rates (0.25-1.0% of fuel feed rate) and for a range of plant availability. Fluxant addition rates were calculated based on viscosity calculations such that fluxant was added at a rate to match the slag viscosity at a gasifier-relevant temperature (1530^{o}C) before and after any sorbent addition. Baseline input values were based on the same operating data as for the initial COE analysis.

The results indicate that even with the increased costs associated with using a sorbent a modest increase in availability (about 1%-2% depending on sorbent feed rate) is enough to offset these costs (see Figure 30). Further increases in availability would result in an overall reduction in COE. Assuming a 0.6 wt% feed rate of sorbent (i.e., a sorbent feed rate of 2X the molar feed rate of metals in the fuel ash), a 5% increase in availability would result in a 2.9% decrease in COE. Based on this data, it appears that using a sorbent would likely have a positive economic effect on the plant.

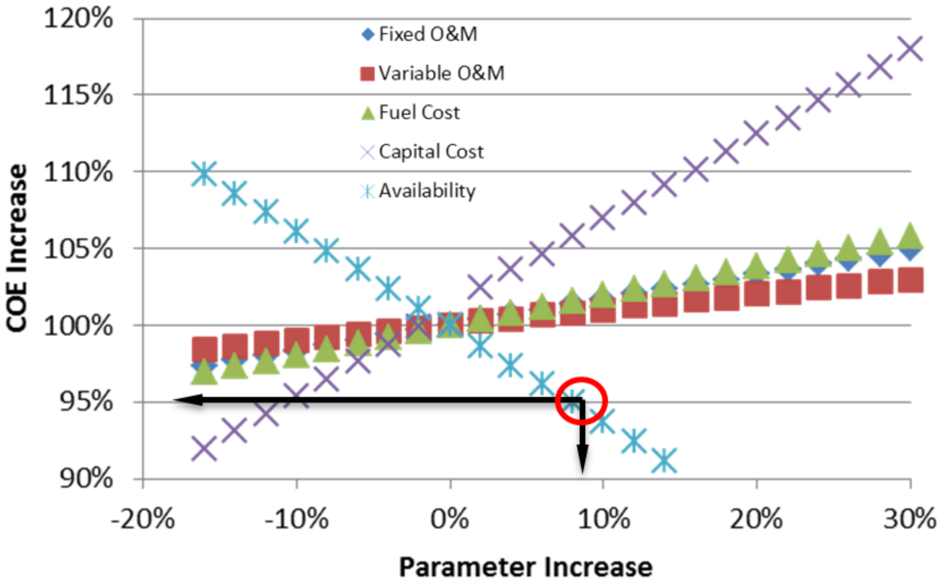


Figure 29. Sensitivity analysis of inputs for the LCAT model on the predicted COE.

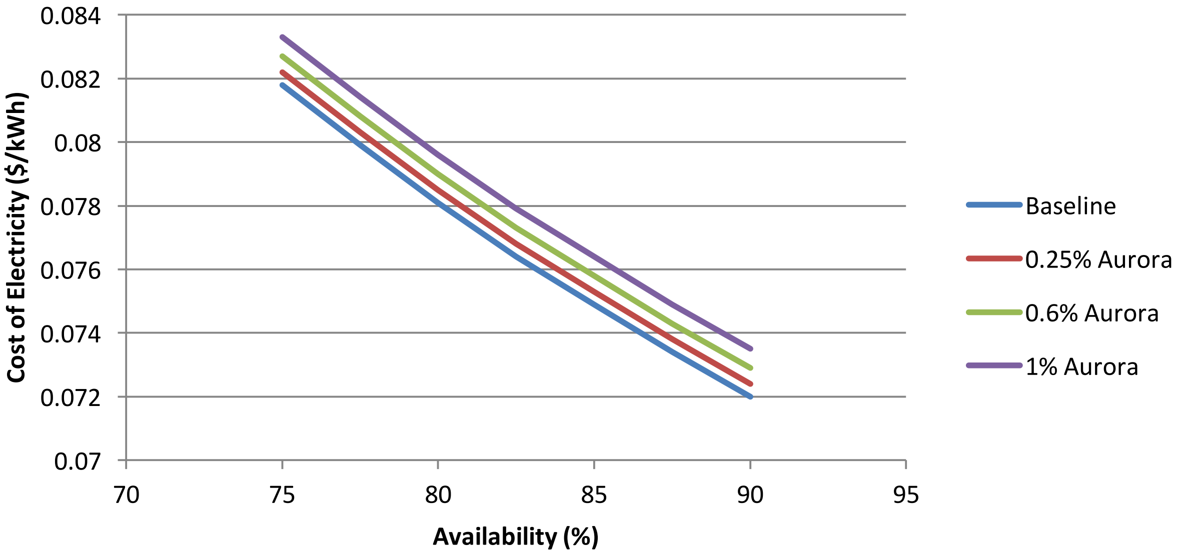


Figure 30. Cost of electricity results for sorbent use. Several sorbent feed rates are represented across a wide range of plant availability. Baseline = no sorbent. X% sorbent implies sorbent feed rate is X wt% of fuel feed rate.

Task 6.0 – Validation of Selected Technology

Objective: Perform a field test of the selected mitigation technology

Nothing to report. Work effort on this Task was not authorized by DOE during BP1 and BP2. This Task was originally planned to be performed in BP3 (see Figure 2 and Table 1).

3.0 SUMMARY AND CONCLUSIONS

All project milestones for BP1 and BP2 were achieved.

REI analyzed two sets of deposit samples from the IGCC plant syngas cooler using several techniques. SEM/EDX analysis shows that the deposits are enriched in sulfur, vanadium, iron, nickel, and zinc, indicating that these elements play a role in the formation of the deposits. Major phases in the deposits include calcium aluminosilicates, metal sulfides, and vanadium-rich phases. The deposits are fairly uniform in composition and do not show evidence of layering. Particle size distribution analysis shows that the particles in the deposits are typically between 1-2 μm in diameter; much smaller than those found in deposits from a typical boiler application. SEM imaging shows evidence that the particles in the deposits sinter and undergo solid state diffusion over time, which leads to increased deposit strength.

Based on our research, REI developed a hypothesis to describe the mechanism for deposit formation. In the hypothesis, some of the metals in the fuel and ash material vaporize when exposed to high temperature. This vapor condenses to form a fine fume as it cools. Due to the small size of the particles, electrostatic and Van der Waals forces can cause the particles to stick to surfaces in areas where the gas flow stagnates.

More than 40 CFD cases were run to simulate formation of deposits in the syngas cooler and to better understand the effects of different parameters (such as tube diameter and spacing) on the rate of deposition. The CFD results showed that larger diameter tubes would decrease the amount of deposition, but would also decrease the overall heat transfer efficiency of the syngas cooler unit. The modeling indicated that using funneled inlet would lessened deposition, but the funnels would also increase the available surface area for deposit formation and could lead to increased plugging.

Pilot scale tests of a candidate sorbent showed that the sorbent was able to capture more than 90% of the submicron particulate in the syngas. REI believes capturing the metal vapor would greatly reduce or eliminate the formation of deposits in the syngas cooler. Techno-Economic-Analysis modeling supports the hypothesis that a small (~2%) increase in availability would cover the costs associated with using a sorbent. A larger increase in availability would result a reduction in the cost of electricity.

A plant test to demonstrate the benefits of using sorbent injection to to mitigate fouling in the syngas cooler used in IGCC plants would be a logical next-step for the development of this technology.

4.0 LITERATURE REFERENCES

1. Adams, B., Fry, A., Senior, C., Shim, H., Wang, H., Wendt, J., Shaddix, C., "Characterization of Oxy-combustion Impacts in Existing Coal-fired Boilers," Contract DE-NT0005288, Interim Report, July 31, 2009.

2. Bockelie, M.J. and Davis, K.A., "A Technology To Mitigate Syngas Cooler Fouling", Presentation to the DOE NETL, SBIR Phase I Contract No. DE-SC0004499, March 24, 2011a.

3. Bockelie, M.J., Davis, K.A., Sarofim, A.F, Precidao, I., Whitty, K., "Toward A Technology To Mitigate Syngas Cooler Fouling", *Proceedings of the International Pittsburgh Coal Conference 2011*, Pittsburgh, PA, September 12-15, 2011b.

4. Bockelie, M.J., "Mitigation of Syngas Cooler Plugging and Fouling", Project Kick-off Meeting held at DOE-NETL Morgantown, West Virginia January 5, 2012a.

5. Bockelie, M.J., "Mitigation of Syngas Cooler Plugging and Fouling", Quarterly Research Performance Progress Report, Cooperative Agreement No. DE-FE-0007952, January 31, 2012b.

6. Bockelie, M.J., "Mitigation of Syngas Cooler Plugging and Fouling", Contract No. DE-FE0007952, Quarterly Research Performance Progress Report, April 30, 2012c.

7. Bockelie, M.J., "Mitigation of Syngas Cooler Plugging and Fouling", Contract No. DE-FE0007952, Quarterly Research Performance Progress Report, July 31, 2012d.

8. Bockelie, M.J., "Mitigation of Syngas Cooler Plugging and Fouling", Contract No. DE-FE0007952, Quarterly Research Performance Progress Report, October 31, 2012e.

9. Bockelie, M.J., "Mitigation of Syngas Cooler Plugging and Fouling", Contract No. DE-FE0007952, Quarterly Research Performance Progress Report, January 31, 2013a.

10. Bockelie, M.J., "Mitigation of Syngas Cooler Plugging and Fouling", Contract No. DE-FE0007952, Quarterly Research Performance Progress Report, April 30, 2013b.

11. Bockelie, M.J., "Mitigation of Syngas Cooler Plugging and Fouling", Contract No. DE-FE0007952, Technical Note, July 2, 2013c.

12. Bockelie, M.J., "Mitigation of Syngas Cooler Plugging and Fouling", Contract No. DE-FE0007952, Quarterly Research Performance Progress Report, July 29, 2013f.

13. Bockelie, M.J., "Mitigation of Syngas Cooler Plugging and Fouling", Contract No. DE-FE0007952, Quarterly Research Performance Progress Report, October 31, 2013g.

14. Bockelie, M.J., "Mitigation of Syngas Cooler Plugging and Fouling", Contract No. DE-FE0007952, Quarterly Research Performance Progress Report, January 31, 2014a.

15. Bockelie, M.J., “Mitigation of Syngas Cooler Plugging and Fouling”, Contract No. DE-FE0007952, Quarterly Research Performance Progress Report, April 31, 2014b.

16. Bockelie, M.J., “Mitigation of Syngas Cooler Plugging and Fouling”, Contract No. DE-FE0007952, Quarterly Research Performance Progress Report, July 31, 2014c.

17. Bockelie, M.J., “Mitigation of Syngas Cooler Plugging and Fouling”, Contract No. DE-FE0007952, Quarterly Research Performance Progress Report, October 31, 2014d.

18. Bockelie, M.J. and Davis, K.A., “A Technology To Mitigate Syngas Cooler Fouling”, Presentation to the DOE NETL, SBIR Phase I Contract No. DE-SC0004499, March 24, 2011a.

19. Bockelie, M.J., Davis, K.A., Sarofim, A.F, Precidao, I., Whitty, K., “Toward A Technology To Mitigate Syngas Cooler Fouling”, *Proceedings of the International Pittsburgh Coal Conference 2011*, Pittsburgh, PA, September 12-15, 2011b.

20. Bockelie, M.J., Davis, K.A., Fry, A.F., Denison, M.K., Shurtz, T., Wang, D., Whitty, K., Celebi, M.C., Jaramillo, C., Wendt, J.O., “Toward A Technology To Mitigate Syngas Cooler Plugging and Fouling”, *Proceedings of the International Pittsburgh Coal Conference 2012*, Pittsburgh, PA, October 15-18, 2012a.

21. Bockelie, M.J., Davis, K.A., Pummill, R., J., Whitty, K., “A Technology To Mitigate Syngas Cooler Fouling”, SBIR Phase II Informal Quarterly Report, DE-SC0004499, May, 7, 2013a.

22. Bockelie, M.J., Celebi, M.C., Davis, K.A., Denison, M.K., Jaramillo, C., Fry, A., Pummill, R., Shurtz, T., Wang, D., Wendt, J.O., and Whitty, K., “Toward A Technology To Mitigate Syngas Cooler Plugging and Fouling”, Presented at the 9th Asia-Pacific Conference on Combustion (ASPACC), Gyeongju, Korea, May 19-22, 2013b.

23. Bockelie, M.J., Davis, K.A., Denison, M.K., Pummill, R., Wang, D., Wendt, J.O., Celebi, M.C., Waind, T., Jaramillo, C., Fry, A., and Whitty, K., “Toward A Technology To Mitigate Syngas Cooler Plugging and Fouling”, Presented at the 38th International Technical Conference on Clean Coal & Fuel Systems, Clearwater, Florida, June 2-6, 2013c.

24. Bockelie, M.J., Davis, K.A., Denison, M.K., Wang, D., Pummill, R., Shim, H., and Wendt, J.O., “Mitigation of Syngas Cooler Plugging and Fouling”, Poster presented at the Gasification Technologies Council 2013 conference, Colorado Spring, Colorado, October 13-16, 2013d.

25. Bockelie, M.J., Davis, K.A., Pummill, R.,, Denison, M.K., Shurtz, T., Wang, D., Whitty, K., Can Celebi, M., Fry, A., Jaramillo, C., Zhongua, Z., and Wendt, J.O., “Mitigation of Syngas Cooler Plugging and Fouling”, *Presented at the International Pittsburgh Coal Conference 2014,* Pittsburgh, PA, October 6-9, 2014b.

26. Bockelie, M.J., Davis, K.A., Pummill, R.,, Wang, D., Wendt, J.O., Can Celebi, M., Fry, A., Jaramillo, C., Waind, T., Whitty, K.,, “Mitigation of Syngas Cooler Plugging and

Fouling”, *The 39th International Technical Conference on Clean Coal & Fuel Systems,* Clearwater, Florida, June 2-5, 2014a.

27. Bockelie, M.J., Davis, K.A., Pummill, R.,, Denison, M.K., Shurtz, T., Whitty, K., Can Celebi, M., Fry, A., Jaramillo, C., Zhongua, Z., and Wendt, J.O., “Mitigation of Syngas Cooler Plugging and Fouling”, *To be presented at the International Pittsburgh Coal Conference 2015,* Pittsburgh, PA, October 5-8, 2015.

28. Bryers, R. W. Fireside slagging, fouling, and high-temperature corrosion of heat-transfer surface due to impurities in steam-raising fuels. Progress in Energy and Combustion Science, 22, pp. 29–120, 1996.

29. Celebi, M.C. and Whitty, K.J., “Characterization of Fine Particulate Material from Syngas in a Pilot Scale Entrained Flow Oxygen Blown Coal Gasifier During Two Stage Gasification,” *Presented at the International Pittsburgh Coal Conference 2014,* Pittsburgh, PA, October 6-9, 2014.

30. Dockter, B., Hurley, J., & Watne, T., Hot-Gas Filter Ash Characterization Project, 1–10. Retrieved from http://www.netl.doe.gov/publications/proceedings/96/96ps/ps_pdf/96pspb2.

31. DOE LCAT, http://www.netl.doe.gov/research/energy-analysis/publications/details?pub=bd406d9f-efe7-42d2-98fd-ee07c96d1456, publication number = NETL/DOE-2012/1566, June, 2012.

32. Environmental Protection Agency. (2006). State Clean Energy-Environment Technical Forum Integrated Gasification Combined Cycle (IGCC) Background and Technical Issues (pp. 1–25). Retrieved from http://www.epa.gov/statelocalclimate/documents/pdf/9_20_revised_final_IGCC_Report_8_24_06.pdf

33. Eslamian, M., Pophali, A., Bussmann, M., Cormack, D.E., Tran, H. N., (2008) “Failure of Cylindrical Brittle Deposits Impacted by a Supersonic Air Jet,” J. Eng. Materials and Tech., Vol. 30, July 2008.

34. Gale, T. K., & Wendt, J. O. L.,”In-furnace capture of cadmium and other semi-volatile metals by sorbents,” Proceedings of the Combustion Institute, 30(2), 2999–3007. 197, (2005).

35. Gallagher, N. B.; Bool, L. E.; Wendt, J. O. L.; Peterson, T. W., Alkali Metal Partitioning in Ash from Pulverized Coal Combustion. *Comb. Sci. and Tech.* **1990**, *74*, 211-221.

36. Gallagher, N. B.; Peterson, T. W.; Wendt, J. O. L., Sodium Partitioning in a Pulverized Coal Combustion Environment. *Proc. Combustion Institute* **1996**, *26*, 3197-3204.

37. Guenther, C., Bennett, J., Shahnam, M., VanEssendelft, D., Granite, E., and Zitney, S., “Overview of National Energy Technology Laboratory R&D Activities and Partnership Opportunities”, Gasification Technologies Conference, San Francisco, CA, Oct. 9th-12th 2011.

38. ImageJ, 2012, software package available at http://rsb.info.nih.gov/ij/index.html

39. Kaliazine, A., Piroozmand, F., Cormack, D. E., and Tran, H. N., (1997) “Sootblower Optimization—Part 2: Deposit Sootblower Interaction,” Tappi J., 80 (11), pp. 201–207.

40. Kang, J., Beverly, R., Porter, D., Leach, W., "Reducing Ash Agglomeration in JEA's CFB Boilers" , Power Magazine, 10/01/2012.

41. Lee, S.-R., Wu, C.-Y., & Andino, J. M. (2007). A Mechanistic Study of Vanadium-Sorbent Surface Interaction at High Temperature. Aerosol Science and Technology, 41, pp. 1063–1075 , 2012

42. Linak, W., Miller, C., & Seames, W. , "On trimodal particle size distributions in fly ash from pulverized-coal combustion," Proceedings of the Combustion Institute, 29, 441–447, 2002.

43. Linak, W. P., Miller, C. A., Wood, J. P., Shinagawa, T., Yoo, J.-I., Santoianni, D. A., King, C. J., Wendt, J. O. L., and Seo, Y.-C., "High Temperature Interactions Between Residual Oil Ash and Dispersed Kaolinite Powders," Aerosol Science and Technology, 38, 900–913,2004.

44. McDaniel, J.E. and Hornick, M., "Polk Power Station IGCC 6th Year of Commercial Operation", Presented at the 2002 Gasification Technologies Conference, San Francisco, 2002a.

45. McDaniel, J.E. and Hornick, M.J., "Tampa Electric Polk Power Station Integrated Gasification Combined Cycle Project, Final Technical Report," Prepared by the Tampa Electric Company for the U.S. Department of Energy, Cooperative Agreement DE-FC-21-91MC27363, August, 2002

46. Mwabe, P. O., & Wendt, J. O. L., "Mechanisms governing trace sodium capture by kaolinite in a downflow combustor." *Symposium (International) on Combustion*, *26*(2), pp. 2447–2453. 1996.

47. Pradyot Patnaik. *Handbook of Inorganic Chemicals*. McGraw-Hill, 2002

48. Landon, T. and Perronnet, M., "Mitigating alkali-related agglomeration, slagging and fouling with engineered combustion additives," Presented at the 38th International Technical Conference on Clean Coal & Fuel Systems, Clearwater, Florida, June 2-6, 2014.

49. Outotek, http://www.outotec.com/en/Products--services/HSC-Chemistry/Calculation-modules/Sim--process-simulation, 2012.

50. Senior, C. L.; Srinivasachar, S. Viscosity of Ash Particles in Combustion Systems for Prediction of Particle Sticking. *Energy & Fuels* 1995, *9*, 277-283.

51. Tillman, D. and Harding, N.S., Fuels of Opportunity: Characteristics and Uses In Combustion Systems, Elseveir, 2004.

52. Wabash River Energy Ltd. (2000). *Wabash River Coal Gasification Repowering Project Final Technical Report*. *Energy*.

53. Wall, T.F.; Lowe, A.; Wibberley, L.J.; Stewart, I.M. Mineral matter in Coal and the Thermal Performance of Large Boilers. *Prog. Energy Combust. Sci*. 1979, 5, 1-29.

54. Wall, T.F.; Bhattacharya, S.P.; Zhang, D.K.; Gupta, R.P.; He, X. The Properties and Thermal Effects of Ash Deposits in Coal-Fired Furnaces. *Prog. Energy Combust. Sci*. 1993, *19*, 487-505.

55. Walsh, P.M.; Sayre, A.N.; Loehden, D.O.; Monroe, L.S.; Beér, J.M.; Sarofim, A.F., Deposition of Bituminous Coal Ash on an Isolated Heat Exchanger Tube: Effects of Coal Properties on Deposit Growth. *Prog. Energy Combust. Sci.* 1990, *16*, 327-346.

56. Walsh, P. M.; Sarofim, A. F.; Beer, J. M., Fouling of Convection Heat Exchangers by Lignitic Coal Ash. *Energy & Fuels* 1992, *6*, 709-715.

57. Walsh, P.M., Xie, J., Poe, R.L., Miller, B.G. and Scaroni, A.W., “Erosion by Char and Ash and Deposition of Ash on Carbon Steel in the Convective Section of an Industrial Boiler,” *J. Sci. Eng. Corrosion* 50(1):82-88, 1994.

58. Wang, H., *Modeling of Ash Formation and Deposition in PC Fired Utility Boilers*. Ph.D. dissertation, Brigham Young University, 1998.

59. Wang, H.**;** Harb, J. N. Modeling of Ash Deposit Growth and Sintering in PC-Fired Boilers. 1997 Engineering Foundation Conference on *The Impact of Mineral Impurities in Solid Fuel Combustion* at Kona, Hawaii, November 2-7, 1997, Edited by Gupta *et al*., pp 697-708, 1999.

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