

HIGH-SODIUM LIGNITE GASIFICATION WITH THE PSDF TRANSPORT GASIFIER

WanWang Peng (205-670-5928, wwpeng@southernco.com), Matt Nelson (205-670-5065, jmmelson@southernco.com),
Roxann Leonard (205-670-5863, rfleonar@southernco.com), Guohai Liu (205-670-5856, gliu@southernco.com),
P. Vimalchand (205-670-5852, pvimalc@southernco.com)
Southern Company, P. O. Box 1069, Wilsonville, Alabama, USA 35186

Robert S. Dahlin (205-670-5068, x2dahlin@southernco.com)
Southern Research Institute, P. O. Box 1069, Wilsonville, Alabama, USA 35186

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Abstract

High-sodium lignite from the Freedom mine in North Dakota was tested in a Transport Gasifier at the Power Systems Development Facility (PSDF). The tests occurred in October 2003 and August 2004 for a total of 445 hours of operation. Due to its high sodium content, the Freedom mine lignite presented unusual challenges to gasifier operations. This paper discusses high-sodium lignite gasification operation and quantifies the potential for deposit formation. The paper also includes the results of extensive lab tests on deposit characterization, briefly covers the mechanics of deposition, and explores the use of additives to prevent deposits from agglomerating in the unit.

During the first use of the high-sodium Freedom lignite in October 2003, agglomerated deposits were formed at various locations in the Transport Gasifier system. An extensive laboratory testing program was carried out to characterize the deposits, to understand the mechanism of the deposit formation, and to test various methods of preventing or minimizing the agglomeration. The results of the deposit analysis and initial lab studies suggested that sodium released from the lignite was deposited on the surface of the sand bed material, resulting in the formation of sticky sodium silicates. Additional laboratory tests indicated that the agglomeration could be avoided or minimized by replacement of the sand with a non-reactive bed material (e.g., coarse coal ash), by operating at slightly reduced temperatures, and by the use of certain types of additives.

In the second use of the high-sodium Freedom lignite in August 2004, several of the remedial procedures that were tested in the laboratory were applied during the gasifier operation. Prior to the introduction of the high-sodium Freedom lignite, much of the sand bed material was replaced with coarse ash from PRB coal, and gasifier operating temperatures were slightly reduced (about 100°F below the temperatures used in the October 2003 run). Dolomite was also fed into the gasifier to help minimize the contact between any sticky particles. By the use of these procedures, the deposition problems that were seen in the October 2003 run were completely eliminated in the August 2004 run.

Introduction

High-sodium lignite from the Freedom mine in North Dakota was tested in a Transport Gasifier at the Power Systems Development Facility (PSDF). The Transport Gasifier is an advanced circulating fluidized bed unit for converting coal into syngas. Since the gasifier operates at considerably higher solids circulation rates, velocities and riser densities than a conventional circulating fluidized bed, the unit exhibits higher throughput, better mixing, and has higher mass and heat transfer rates than typical gasifiers. Over 6,400 hours of gasification have been achieved at the PSDF with different fuels, including PRB and various bituminous coals and lignites, in both air- and oxygen-blown operations.

Gasification tests with the Freedom high-sodium lignite were conducted at the PSDF in October 2003 and August 2004 for a total of 445 hours of gasifier operation. The operating experience and deposition problems encountered have been discussed in detail by Davis et al [1]. This paper focuses on the laboratory and fluidized bed testing that was conducted to characterize the deposits, to understand the mechanism of the deposit formation, and to test various methods of preventing or minimizing the agglomeration.

Characterization of agglomerated deposits

Agglomerates and agglomerated deposits formed in several locations in the gasifier loop during the October 2003 gasifier run. Eventually, the deposits blocked the cyclone loop seal and prevented the circulation of solids back to the gasifier. After the run, the deposit that was present in the loop seal had to be removed by rodding it out. The photo below shows some of the large chunks which were soft that dropped out as the deposit was broken apart.



Figure 1. Chunks of Agglomerated deposits removed from cyclone loop seal.

Although the chunks were black, chemical analysis showed that they actually contained only 0.1 to 0.4 wt % carbon. Microscopic examination revealed that some of the particles were black, but most of them appeared to be glassy sand, sorbent, and ash (Figure 2). More detailed examination showed that the black particles were actually sand particles that were presumably glued with a thin outer layer of char (Figure 3).



Figure 2. Micrograph of deposit showing glassy sand grains, sorbent and ash.



Figure 3. Micrograph showing sand grain covered with fine char particles.

The chunks of loop seal deposit were ground as fine as possible in a mortar and pestle, and the ground powder was used in a variety of lab and fluidized bed studies designed to understand the mechanism of the agglomeration and to evaluate various corrective measures. Bulk chemical analyses confirmed that the deposit contained about twice as much silica as the high-sodium lignite ash on an ignited basis (35 to 41 wt % SiO_2 in deposit versus 17 to 21 wt % SiO_2 in lignite ash). Therefore, it is clear that the deposit was enriched in sand which was the start-up bed material.

Studies of Agglomeration and Possible Corrective Actions

Experiments with heated deposit samples. Samples of the ground loop seal deposit were heated in a lab muffle furnace in air to 1400, 1600, and 1900°F (760, 870, and 1040°C) to see if they would reconsolidate. As the treatment temperature was increased, an increasing degree of sample consolidation was observed. Some degree of sintering and neck formation between particles was noted even at the lowest temperature and became more pronounced as the temperature was increased. The particles also became progressively glassier and appeared to be largely amorphous at the highest temperature. The micrograph below shows a close-up of a neck formed between two sand particles from the gasifier standpipe sample.

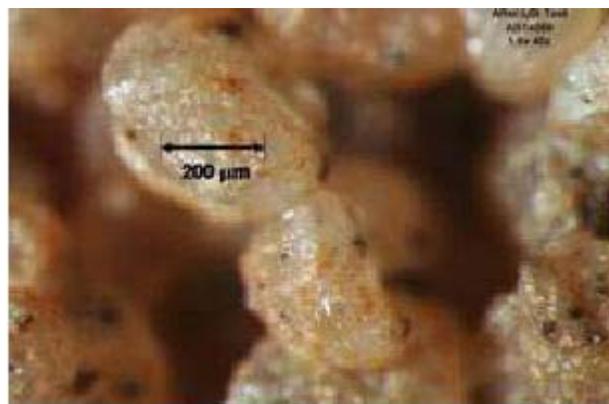


Figure 5. Close-up of neck formed between two sand grains.

Energy-dispersive x-ray analysis confirmed that the particles were almost pure silica with small amounts of impurities. The neck region between the particles also contained silica and was

enriched in sodium. Based on this observation, we speculated that the sintering may involve the formation of low-melting sodium silicates.

Experiments with sintering in sand/sodium mixtures. In tests with silica sand and sodium (in the form of NaOH solution) in varying amounts, the primary deposit product is undoubtedly sodium silicate. It is interesting that the addition of 5 wt % sodium resulted in extensive melting, since the loop seal deposit contained 6 to 7 wt % sodium as the element (8 to 10 wt % as Na₂O). Since the gasifier operating temperatures were actually somewhat higher than the temperature used in this experiment, it is very likely that sticky sodium silicate would have been formed in the gasifier under the operating conditions.

Experiments with various additives to prevent agglomeration. The feasibility of using an inert powder to block the agglomeration was tested with three different materials, dolomite, calcite, and coarse coal ash. Also, dolomite, calcite and minerals in coal ash can potentially react with sodium silicates to form complexes with melting temperatures higher than the gasifier operating temperatures. The tests were done by mixing the pulverized material with the ground loop seal deposit and heating the mixture to 1700°F (930°C) for five hours in a crucible in a muffle furnace.

Under the above conditions, the loop seal deposit with no additives was completely reconsolidated. The mixtures with 5 and 10 wt % dolomite were less consolidated, but contained several agglomerated chunks that were on the order of ¼ to ½ in. (0.6 to 1.3 cm) in size. There was essentially no consolidation in the mixture containing 20 wt % dolomite.

Similar experiments were conducted with coarse calcite having a mean particle size of 700 µm. In these tests, the deposit, the raw calcite, and various mixtures of deposit with calcite were heated to 1700°F (930°C) for five hours. The calcite prevented reconsolidation using a concentration of only 10 wt %. Because of the large size of the calcite particles, the number ratio of calcite to deposit particles was very low. Therefore, it seems unlikely that the calcite particles could be physically blocking the agglomeration of the sticky deposit particles. The phase diagram for the system of Na₂O, SiO₂, and CaO shows that the addition of CaO to the Na₂O-SiO₂ system tends to shift the system toward higher melting points, thereby reducing the tendency to form sticky phases.

Ash from the PRB coal was also shown to be an effective additive to reduce the reconsolidation of the loop seal deposit. This suggests one possible approach to dealing with the agglomeration problem – replace the start-up sand bed material with coarse coal ash, reducing the amount of silica available to react with the sodium vapor, and thereby reducing the formation of sticky sodium silicate.

Additives that scavenge sodium vapor – We evaluated three different sorbent materials that were known to adsorb or react with sodium vapor at high temperatures: sand flour, kaolinite, and a paper mill byproduct that contained kaolinite. The sand flour was a very fine grind of sand having a mean size of 14 µm. The kaolinite was a pure form of the mineral that is produced commercially for use in paint pigments. The mean particle size of the kaolinite was 5.5 µm. The paper mill byproduct was a decarbonized form of de-inking sludge that contained about 50 wt % kaolinite. It had a mean particle size of about 15 µm.

All of these materials were so fine that there would be very little retention of the additive in the gasifier loop. The lack of retention in the gasifier loop is actually a desirable feature with these materials, because the sand flour and the kaolinite will tend to form sticky sodium silicates (and sodium aluminosilicates in the case of the kaolinite). Therefore, they would actually exacerbate the agglomeration problems if they were retained in the gasifier loop. If, on the other hand, they are carried out of the system, it might be possible to capture some of the sodium vapor and mostly remove it from the gasifier loop in the first pass before it can accumulate and cause deposition.

All three of the sodium-scavenging additives were tested by placing a relatively thin layer of the additive over a thicker underlying layer of the ground deposit and heating the layers to 1700°F (930°C) for five hours. In the case of the sand flour and the kaolinite, the top layer became completely consolidated due to uptake of sodium vapor that was released from the underlying layer of deposit. These results suggest that both sand flour and the kaolinite will capture sodium vapor at the temperatures of interest. Removal of the fine sticky product from the gasifier loop will minimize deposit potential in the gasifier. Since the paper mill byproduct contains about half kaolinite, it probably also captured some sodium, but it did not consolidate due to the presence of other components. Nevertheless, it may be an attractive sorbent material if it can remove some sodium without agglomerating.

Fluidized Bed Tests

A mini reactor unit built for catalyst and absorbent screening tests with bottled gases as well as coal syngas was modified for parametric deposit characterization tests. The mini reactor is 1.5" in (3.8 cm) in diameter and 3 ft (0.9 m) in height imbedded in an external heating furnace. It could be operated up to 1800°F (980°C) and 14 psig (100 kPa). The mini reactor was protected from directly contacting the test sample by adding an easily removable internal pipe with screen at its bottom for even gas distribution. The internal pipe was attached to the top of the reactor cap, which ensures that all the gas flowing through the reactor will pass through the test sample. The reactor was heated at 200 to 400°F/min (110 to 220°C/min) to test temperatures where it was maintained for one to two hours. The reactor was then cooled and the sample was taken out for analysis.

One set of mini reactor tests focused on operations at higher temperatures. The deposit from the Transport gasifier loop seal was ground and heated to temperatures between 1650 and 1750°F (900 to 950°C). The ground deposit reconsolidated even though the bed was fluidized with nitrogen. High sodium lignite ash was carefully generated at relatively low temperatures in order to lessen the potential of any sodium loss. The lignite ash itself did not show any deposit tendency when heated up to 1750°F (950°C) in the mini reactor. However, mixtures containing lignite ash and sand began to consolidate loosely in 1650 to 1750°F (900 to 950°C) temperature range. Dolomite addition reduced the extent of consolidation, likely due to reactions with alkali compounds leading to high melting temperature compounds.

Tests with a mixture of high sodium lignite ash and PRB coal ash in the 1650 to 1750°F (900 to 950°C) temperature range showed no consolidation, suggesting that the PRB coal ash can be used as a start-up bed material instead of quartz sand. Both PRB coal ash and lignite ash lead to hard

consolidated deposits when mixed with small amounts of simulated sodium compounds. This suggests that the accumulation of sodium in the form of silicates in the gasifier will eventually lead to deposits. Addition of dolomite lessens the potential of accumulating low melting temperature silicates in the gasifier.

Conclusions

The studies described above suggest that the deposition problems encountered in the October 2003 run were most probably related to the formation of sticky sodium silicates through the interaction of sodium from the high-sodium lignite and the silica in the sand bed material. The studies also provide evidence to support the use of additives to either block the agglomeration of sand particles covered with sticky sodium silicates or to reduce the formation of the sodium silicates on the bed material by scavenging the sodium vapor before it can react with the sand. If coarse PRB ash could be used as the gasifier bed material in lieu of sand, it would effectively reduce the silica content of the bed material from 100 % to about 20 %, and thereby greatly reduce the potential to form sticky sodium silicates. The use of coarse PRB ash as a bed material and the use of slightly reduced operating temperatures were tested in a subsequent gasifier run in August 2004. These changes were shown to effectively eliminate the agglomeration and deposition problems that had occurred previously in October 2003.

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