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PREVENTING AGGLOMERATION PROBLEMS DURING GASIFICATION OF HIGH-SODIUM LIGNITE

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Introduction and Background

Previous gasification studies have shown that sodium vapor released from high-sodium lignites can react with silica to form sticky sodium silicates.[1,2,3] These sticky sodium silicate compounds naturally tend to glue particles together leading to the formation of agglomerated deposits in the gasifier. Laboratory studies reported in our previous paper suggested that the formation of these sticky sodium silicates was responsible for the agglomeration and deposition problems encountered during the use of high-sodium lignite in a previous test run (TC13) at the Power Systems Development Facility.[4] The previous laboratory studies also suggested that the agglomeration could be minimized by eliminating the sand bed material, reducing the gasifier operating temperature, and introducing an inert particulate material (e.g., dolomite or limestone) to reduce the contact between sticky particles. To take advantage of these observations, a subsequent test run (TC16) was performed with the sand bed material eliminated, the gasifier operating temperature limited to about 930°C (1700°F), and with the addition of dolomite into the gasifier recycle loop. With these remedial steps in place, the high-sodium lignite was successfully gasified without any signs of agglomeration or deposition problems. After the successful gasification run in TC16, another run (TC21) was attempted with the same lignite. In TC21, however, the sodium content of the lignite was somewhat higher (about 8 to 9 wt% as Na_2O in the ash versus about 6 to 7 wt% in TC16). With the higher sodium content, the problems with agglomeration and deposition recurred.

Analysis of Agglomerated Deposits

After TC21, extensive deposition was found in the gasifier lower mixing. Examination of the deposits by scanning electron microscopy (SEM) revealed that the particles in the deposit were bonded together (Figure 1). The predominant elements detected by energy-dispersive x-ray (EDX) analysis were Mg, Ca, Al, Si, Fe, and Na (Figure 2). The high concentrations of Mg and Ca were attributed to the dolomite addition; while the other elements were expected components of the lignite ash.

To better understand the nature of the deposit formation in TC21, samples of the deposits taken from the lower mixing zone of the gasifier after TC21 were subjected to various lab tests. First, the deposit chunks were pulverized and heated to various temperatures to determine the minimum temperature required for reconsolidation. These tests showed that the deposits reconsolidated even at temperatures as low as 540°C (1000°F). Given the relatively low temperatures at which reconsolidation was observed, it was clear that reduction of the gasifier operating temperature alone would not be a viable means of preventing the agglomeration seen in TC21. Moreover, because of the relatively large reconsolidation tendency of the TC21 deposit, it was clear that any additives used to prevent agglomeration would need to be even more effective than the dolomite used in TC16. With these factors in mind, a series of experiments was conducted to evaluate various additives that might help minimize agglomeration and deposition problems. The additives tested included: dolomite, calcite, sand flour, amorphous silica fume, bauxite, calcined bauxite, vermiculite, kaolinite, fine kaolin, waste-derived kaolinite, and meta-kaolin.

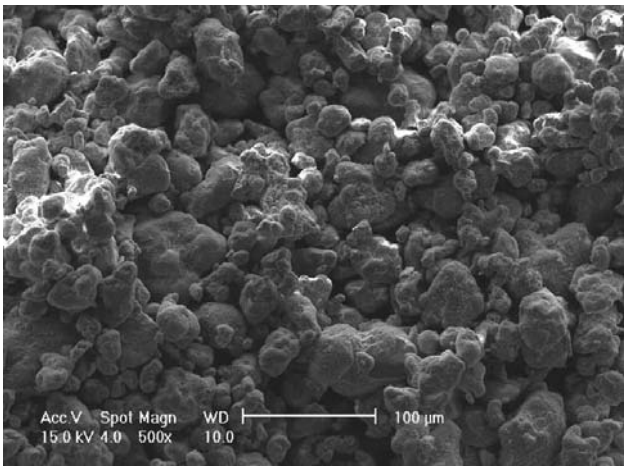

Figure 1. *SEM photograph of TC21 deposit*

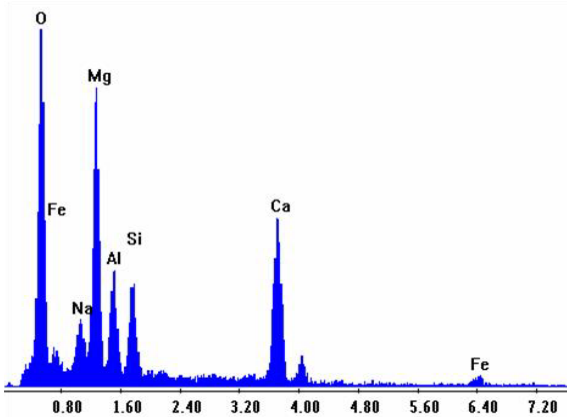

Figure 2. *EDX analysis of TC21 deposit*

Additive Tests

In the past, testing has shown that dolomite and calcite act mainly as inert materials to prevent contact between particles that are covered with sticky sodium silicates.[4] Unlike the dolomite and calcite, the other additives listed above will react with sodium and form sodium silicates, aluminates, and aluminosilicates. While the sodium silicate alone would be quite sticky, it was hoped that the presence of the aluminates and aluminosilicates in these materials would increase the softening temperature sufficiently so that the other additives would not be sticky at gasifier temperatures. This postulate was confirmed for several of the additives tested in a muffle furnace at temperatures up to 982˚C (1800˚F). The additives that were able to capture sodium vapor without consolidating included the meta-kaolin, vermiculite, two types of the silica fume, and bauxite. The other additives that were tested (sand flour, kaolinite, fine kaolin, and calcined bauxite) became sticky and consolidated when exposed to sodium vapor. A coarse form of meta-kaolin (mean size 920 microns) was able to prevent reconsolidation of deposits at temperatures as high as 982˚C (1800˚F). SEM/EDX analysis confirmed that the metakaolin was able to capture sodium vapor without consolidation. Based on these results, the meta-kaolin was selected as the most promising additive for a subsequent gasification test.

Gasification Test with Meta-Kaolin Additive

Based on the laboratory test results, it was decided to conduct another gasifier run with the high-sodium lignite, this time with the meta-kaolin used as an additive. The gasification run (TC23) was started with PRB coal to replace any sand bed material with coarse coal ash. After the sand was eliminated from the system, the gasifier was transitioned to high-sodium lignite feed with the simultaneous addition of the meta-kaolin. The meta-kaolin was added with the lignite at a rate roughly equivalent to the ash content of the lignite (~10 wt %). During the run, the gasifier operating conditions and solids samples were closely monitored to detect any signs of agglomeration or deposition. As shown in Figure 3, microscopic examination of the large meta-kaolin particles in the gasifier standpipe samples showed no signs of agglomeration, even when baked at 982˚C (1800˚F).

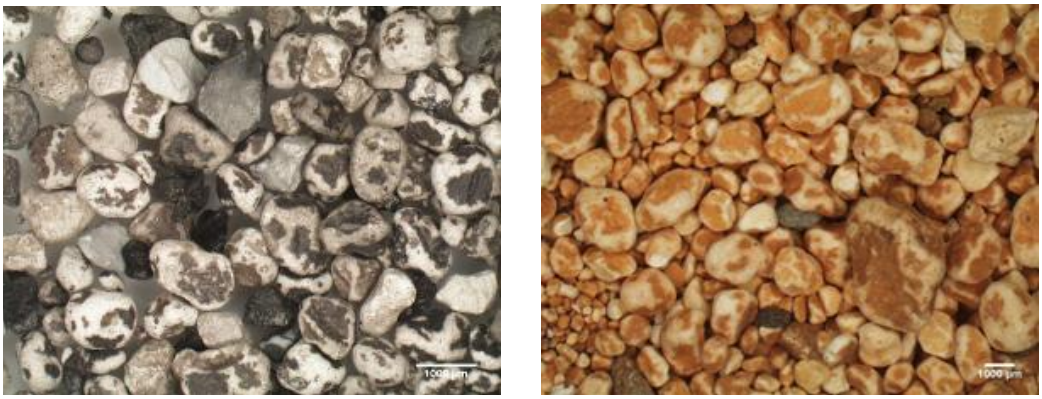

Figure 3. *Large meta-kaolin particles in gasifier standpipe samples before baking (left) and after baking (right) (Note that there is no evidence of agglomeration)*

To determine whether the meta-kaolin had captured sodium, the meta-kaolin particles in the gasifier standpipe samples were analyzed by EDX, and the same type of analysis was performed on the raw meta-kaolin for comparison. Figure 4 shows a comparison of the EDX spectra. The comparison of the EDX spectra clearly shows that the meta-kaolin particle in the standpipe sample has captured sodium. This analysis was obtained from an area of the meta-kaolin particle surface that was not coated with ash. In cases where spectra were obtained from ash-coated surfaces, the spectra showed much higher peaks for calcium, iron, and other elements associated with the ash. In those cases, it was difficult to determine how much of the sodium was associated with the ash as opposed to the meta-kaolin surface. However, in cases where there was no ash coating on the meta-kaolin, there was clear evidence of sodium capture.

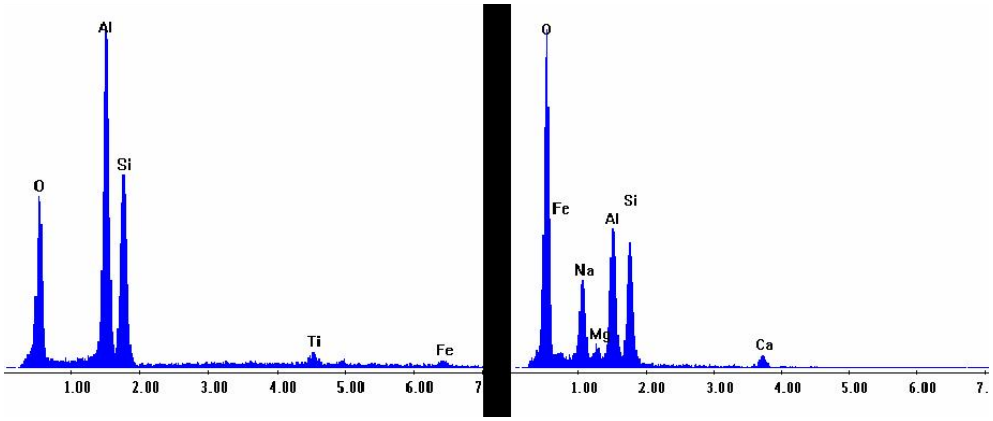

Figure 4. *EDX spectra from raw meta-kaolin (left) and meta-kaolin particle in gasifier standpipe sample (right) (Note evidence of sodium capture in meta-kaolin from gasifier standpipe)*

Even in these particles that had captured significant sodium, there was no evidence of sintering between particles. Therefore, it appears that the larger meta-kaolin particles can capture sodium without become sticky and agglomerating. This observation is consistent with the findings of Kosminski et al[5] who reported that kaolin reacts with sodium under gasification conditions to form solid nepheline ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$) without the formation of any liquid silicates.

Conclusions

The addition of coarse (minus 14-mesh, 920-μm mean size) meta-kaolin successfully prevented agglomeration and deposition problems during gasification of high-sodium lignite at a maximum operating temperature of 927°C (1700°F). Laboratory tests suggested that the use of the meta-kaolin additive may allow even higher operating temperatures -- up to 982°C (1800°F) -- but additional gasifier testing would be needed to confirm that. Particle size appears to be a critical parameter, since the laboratory tests showed extensive consolidation in the much finer forms of kaolin (e.g., hydrous kaolin with a mean size of 4 μm). Fouling of the primary gas cooler also provided evidence to support this conclusion. The problem with fouling of the gas cooler by fine meta-kaolin particles could be addressed by using a quench cooler instead of a tubular heat exchanger. The quench cooler (basically a water spray) could be used to cool the gas to a point where the kaolin is no longer sticky, and then a downstream shell-and-tube heat exchanger could be used for heat recovery.

It should be noted that the meta-kaolin was not the only additive that was found to capture sodium without consolidating in laboratory studies. This was also true of the vermiculite, two types of the silica fume, and bauxite. Gasifier tests would be required to determine whether these additives are acceptable alternatives to the meta-kaolin. The other additives that were tested (sand flour, kaolinite, fine kaolin, and calcined bauxite) became sticky and consolidated when exposed to sodium vapor.

Economic analyses are needed to determine whether the addition of the meta-kaolin is economically feasible. The purchase price for the material used in this study was approximately $100 per ton (~11¢ per kg). With a lignite containing 10% ash by weight, the amount of meta-kaolin used in the gasifier would be approximately 0.1 kg per kg of coal. This rate of addition would effectively add $10 per ton (~1.1¢ per kg) to the cost of lignite gasification. This additional cost would be significant, but it may be justified if it allows the use of low-cost lignite fuels that cannot be gasified otherwise. Also, there may be less expensive forms of kaolin available. For example, according to the U. S. Geological Survey's Mineral Commodity Summaries for January 2008, the bulk price of ball clay and bentonite is $48 per ton (~5¢ per kg), which would effectively add about $4.80 per ton (~0.5¢ per kg) to the cost of the lignite.

It may also be possible to further reduce the cost by using certain low-value waste materials that contain kaolin. For example, certain de-inking sludges from paper mills contain approximately half kaolin/kaolinite mixture. Since these materials are waste products, it may be possible to obtain them for a much lower price than the meta-kaolin. We have performed preliminary lab tests with two different types of kaolin-containing de-inking sludges. Unfortunately, one of these materials consolidated while the other did not consolidate. Further analysis will be required to understand the reasons for the different behavior of these two materials.

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