Custom reagents reduce slagging

What drives slag formation in coal-fired utility-scale furnaces and how can it be dealt with? CoalTreat reagents are applied pre combustion to adjust fuel chemistry and have proved highly effective for solving furnace slag problems, as demonstrated by four case studies.

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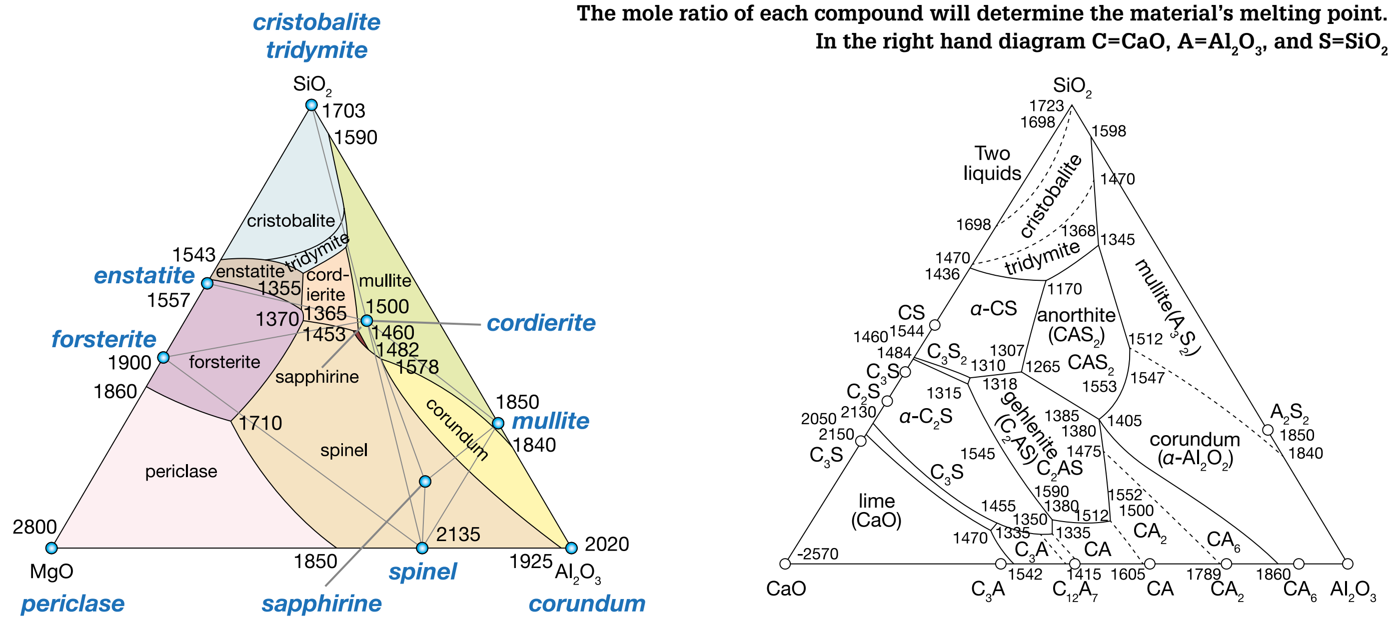


Figure 1. The MgO-Al_2O_3-SiO_2 three-phase diagram is shown on the left and the CaO-Al_2O_3-SiO_2 diagram on the right. The mole ratio of each compound will determine the material's melting point. In the right hand diagram C=CaO, A=Al_2O_3, and S=SiO_2

Fuel flexibility is essential for coal fired power plants to remain competitive in today's power generation market. Firing lower quality fuels is often an effective way to reduce generating costs, particularly when the plant has surplus air quality control equipment capacity. For example, many generators in the USA are leveraging high sulphur Illinois Basin (ILB) and Northern Appalachian (NAP) coals while others are blending Powder River Basin (PRB) coals to meet stringent mercury and acid gas emission limits. However, many opportunity fuels often introduce boiler reliability concerns, such as increased boiler slagging and fouling, into the economic equation.

In response to these industry-wide problems, Environmental Energy Services (EES) developed CoalTreat, a pre-combustion, fuel chemistry innovation that has proven highly effective in reducing furnace slagging and heat transfer surface fouling.

How does slag form?

Many factors drive slag production in coal-fired boilers, such as coal particle combustion temperature, residence time, oxygen present in the furnace, sulphur species, and the presence of metals. The type of coal being burned also plays an important role in determining the type of slag formed. For example, PRB coal contains high levels of calcium whereas bituminous coals have almost no calcium, which has an impact on the type of slag formed.

Most of the research on high temperature slagging is based on the many crystal compounds that form from the decomposition of clays and other alumina-silicates and the effect of elements like calcium, iron, sodium and potassium on ash viscosity and melting temperatures. For example, particles high in silica will tend to form amorphous slags (amorphous glass at high temperatures) while those low in silica will crystallise. The removal methods for each are different. There are three other important slag properties that must be considered: melting point temperatures; pyritic sulphur formation; and sintered ash deposits.

Figure 2. Processing pyrite in coal combustion. "Excluded" and "Included" pyrite follow slightly different oxidation processes

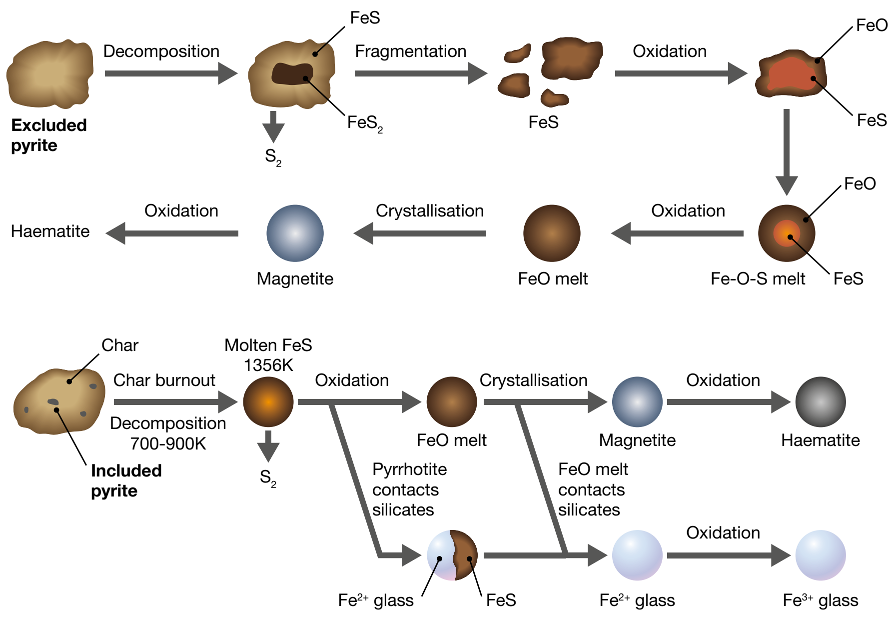


Figure 3. A high temperature probe duplicates boiler tube surface temperatures to simulate deposit bond and deposition rate. Deposits are then collected and analysed by a third-party laboratory. The tests are repeated to optimise reagent type and dosage

- ***Melting point temperature.*** The MgO-Al_2O_3-SiO_2 three-phase diagram is used to determine the structure of the compound formed for known mole fractions (Figure 1, left). The ratio of the different metal contents and the oxidation/reduction state of the furnace will determine which compounds are formed in the slag and their melting points. In theory, magnesium may be added to alter the melting point of an alumina-silicate-based slag to raise the ash softening temperature. In practice, there may be interactions with many metals and combustion conditions, especially the distribution of oxygen in the furnace, that are critical factors in the analysis.

Pure lime (CaO) has a high melting point, but changes in the mole ratios of silica and alumina in the ash will decrease the melting point temperature. Most of the alumina silicate formations in slag are amorphous, meaning it is without a crystal shape. If a brittle (or friable) crystalline structure forms then the slag is very likely to fracture during soot blowing. Anorthite, located in the centre of the CaO-Al_2O_3-SiO_2 diagram (Figure 1, right), has a brittle crystalline structure with a melting temperature of 2836°F. The compound is formed when two moles of silicon dioxide react with one mole each of aluminum oxide and calcium oxide. Fortuitously, most bituminous coals have a silica to alumina ratio of 2 to 1 and will form anorthite in the presence of calcium. However, bituminous coals generally lack calcium. If a highly reactive form of calcium is added to the combustion zone then the more easily fractured anorthite is formed.

- ***Pyritic sulphur formation.*** Sulphur and iron also exist naturally in coal as pyrite (FeS_2). During combustion, pyrite will either: remain unchanged (if large particles); convert to Fe^{3+} sulphates; or oxidise fully to haematite (at 932°F) releasing pyritic sulphur, which will react with any alkalis, Ca, or Mg present in the furnace. The oxidation process path taken is strongly dependent on particle size, which is a function of the unit's mill performance. If a coal particle is too large then it will not have sufficient time to completely combust (Figure 2).

Our tests have shown that when pyrite is reacted with the alumina-silicates in the ash, iron migrates into the Al-Si structure. Consequently, adding a highly reactive form of calcium to the combustion process will efficiently capture pyritic sulphur, forming high melting point haematite instead of the low melting point ferrous sulphate. The importance of this observation will become apparent shortly.

- ***Sintered ash deposits.*** Sodium sulphate melts at 1622°F while mixed alkali-metal sulphates can form a molten phase at much lower temperatures (~1200°F), which will condense on boiler tube surfaces. The result is a sticky layer of ash on tubes, which attract more fly ash creating a build up of slag. As the layer grows and moves away from the insulating effects of the steam tubes, the temperature increases causing the new particles to melt and flow together (known as viscous flow sintering). Adding magnesium or calcium to the mixture forms their respective sulphates which significantly increases the mixture's melting point (>2200°F) thus eliminating the sticky first layer of slag formed by alkali deposition, stopping further deposit growth.

A new direction: pre-combustion coal treatment with customised reagents

In practice, controlling furnace slagging begins with optimising mill performance to provide the expected coal fineness and proper tuning of the plant. Coal ash chemistry modifications are more effective and far more economic once the unit has been properly tuned.

The next step is furnace slag testing. Measuring and mapping the oxygen content within the combustion zone and the temperature distribution in the upper furnace is critical. Slag samples are collected on the surface of a high temperature probe (HTP) and analysed to determine the proper reagent type and dosage necessary to alter the ash chemistry of the coal to ease removal from furnace tubes (Figure 3). An example of the HTP before and after treatment is shown in Figure 4. Scanning electron microscope (SEM) and X-ray diffraction (XRD) analyses may also be used to identify the crystal composition of the slag. There are a variety of reagents, CoalTreat 300, 600, 710, 780, which may be selected or mixed depending on the structure of the slag.

The method of application must be selected once the proper chemical reagent and application rate are determined. Chemicals must be added to the coal prior to combustion for the most efficient reaction. Therefore, reagents should be applied to coal on the main transfer conveyor when bunkering or to coal just prior to entering the mills. The application spray pattern is

Figure 4. The baseline high temperature probe (HTP) testing at a PRB-fired 640 MW opposed wall furnace produced a heavy layer of black glass that adhered to the probe (top). The coal was pretreated with CT-300 at an initial "shock" dosage and later optimised to a reduced maintenance dosage. HTP testing was repeated one day later and the coating on the probe was more porous, friable, and cracked off as it was removed from the inspection port (bottom), confirming the sticky alkali layer of slag was prevented from forming

of minor importance since the mills handle final mixing of the reagent with the coal.

Four case studies

The following four case studies illustrate the excellent results attained when a properly designed reagent is applied to different types of coal fired in different furnace designs.

Case study 1

The utility wished to demonstrate that its units were capable of burning 100% Rochelle North Antelope PRB coal. The low sulphur, low pyritic iron and high calcium content of PRB coals make them relatively simple to treat. Testing revealed that the highly reactive magnesium compound in CT-300 would react with a small amount of sulphur to keep the iron out of the glassy slag melt. The result is an increase in melting point temperature by formation of a high temperature magnesium alumina spinel ($MgAl_2O_4$).

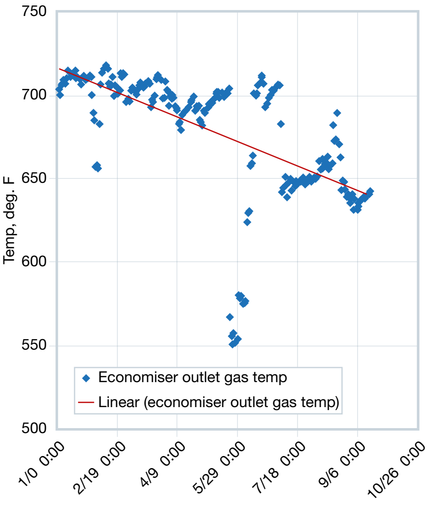
A relatively high dosage "shock treatment" was chosen to start, followed by a reduced "optimised" dosage for the remainder of the demonstration. Overdosing must be monitored as it can cause slag fluxing (lowering the viscosity) and create additional slag stickiness at higher temperatures.

HTP testing confirmed the effectiveness of CT-300 with the collected slag deposits and fly ash fusion temperatures increasing by more than 100°F over baseline. The furnace remained clean throughout the demonstration period.

Case study 2

The utility wished to demonstrate that its units were capable of burning 100% Antelope PRB coal. The utility's experience was that burning this coal would quickly force a 50 MW unit derate due to excessive slag build up in the upper furnace and on boiler walls. Analysis of the coal followed by subsequent treatment and HTP testing indicated that CT-300 would resolve furnace slag issues. Post-test boiler DCS data confirmed the results. Magnesium reacted with sulphur in the flame, leaving the iron to oxidise and remain out of the slag melt. HTP testing showed fusion temperatures increased over 200°F. A closer look at the unit's DCS data, particularly the economiser outlet gas temperatures, revealed the positive effect of reduced furnace slag. The economiser exit temperature dropped 50°F in less than 24 hours following treatment (Figure 5). The unit was able to return to full load (500 MW) for the remainder of the demonstration. The utility has since standardised the CT-300 treatment regimen and has installed a permanent treatment system. Treatment was expanded to include slag control with ILB/PRB coal blends with the objective of increasing the plant's net output.

Figure 5. Economiser outlet gas temperatures dropped 50°F shortly after CT-300 treatment began. The unit recovered the 50 MW lost due to furnace slagging.

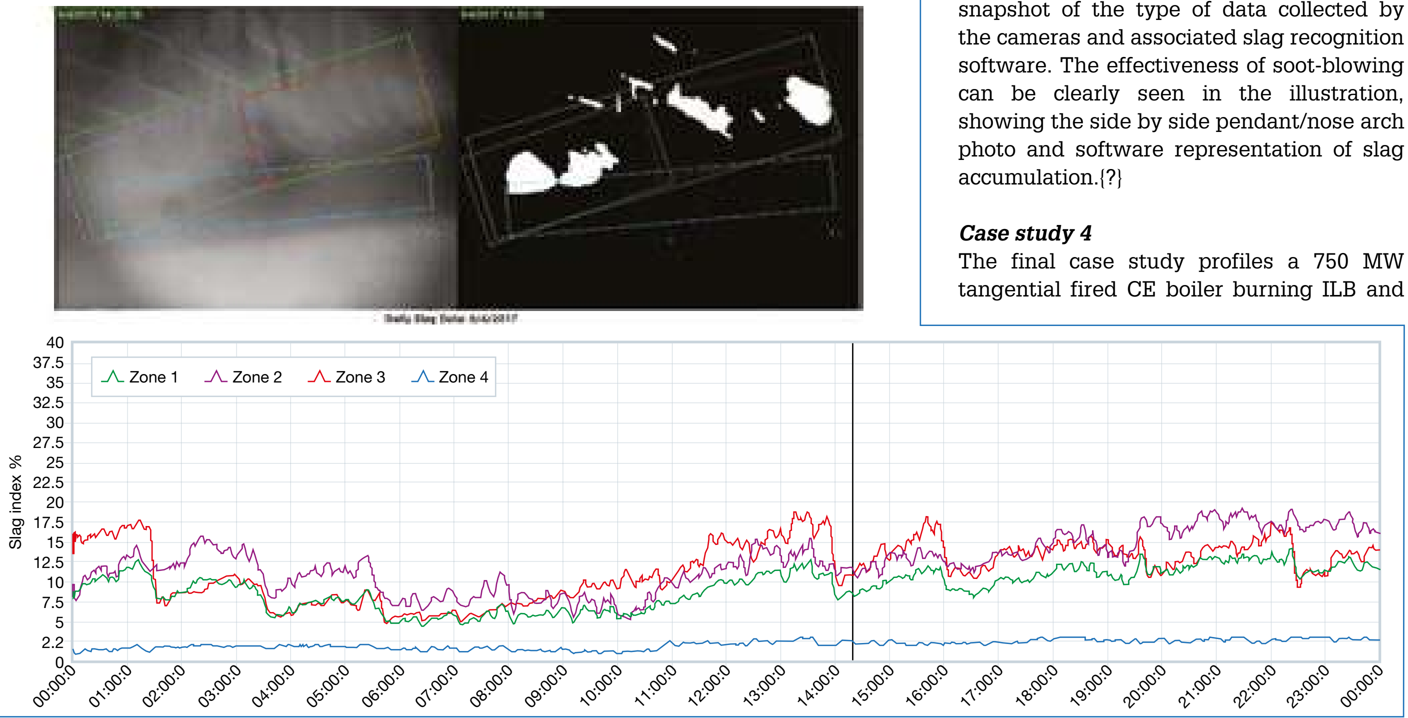


Case study 3

This case study focuses on a 650 MW PC unit that was challenged by burning high levels of ILB coal along with some of the highest slagging NAPP coals known to EES. The station is strategically positioned alongside the Ohio River, receiving all coal via barge. EES participated in an EPRI sponsored two week demonstration to test the use of boiler cameras fitted with slag detection software to compare furnace buildup of slag generated from high iron/high alkalis, low fusion temperature ILB/NAPP coal blends. The blends are extremely challenging but provide the station with lower fuel costs. The station experienced frequent forced derates and the need for online washing numerous times per year prior to the demonstration. The demonstration was designed to compare results from the slag cameras for blends burned with, and without additives with appropriate field adjustment of CoalTreat dosages.

The station was able to burn very high Hansel-Halfinger Index coal blends at a consistently high load for five consecutive days with CoalTreat. The pendant and nose arch areas were effectively maintained by normal soot-blowing during these challenging coal burns. Slag cameras were found to be extremely useful tools for monitoring slag deposits over the course of the demonstration. Figure 6 provides a snapshot of the type of data collected by the cameras and associated slag recognition software. The effectiveness of soot-blowing can be clearly seen in the illustration, showing the side by side pendant/nose arch photo and software representation of slag accumulation.{?}

Figure 6. IR camera photo of tube bank and soot blower performance trend

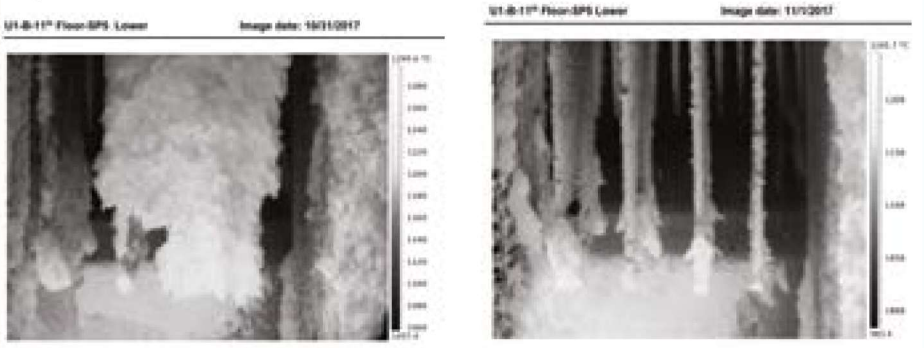


Case study 4

The final case study profiles a 750 MW tangential fired CE boiler burning ILB and

NAPP coals with mid-high sulphur and high iron content. The unit was consistently derated due to slagging, with bridging in the furnace pendants just above the nose arch of the furnace. Portable IR cameras were used by the plant to monitor slagging. EES was called in to treat a dirty furnace with the goal of restoring the boiler to normal operating parameters. Initial treatment began with a blend of CoalTreat additives and was later optimised using HTP and visual observations. The trial was successful, and the plant continues to use CoalTreat to ensure reliability and to maximise efficiency. Figure 7 shows before and after CoalTreat photos.

Figure 7. Lower 11th floor, before and after treatment



Treatment plan economics

Each unit and fuel combination is unique, so the cost of treatment is site specific. However, experience provides some general guidance. For estimating purposes, the cost of CoalTreat ranges from $ 0.35 to $ 1.20/ton of coal treated depending on the type of coal, the complexity of the CoalTreat ash correction formulation, and the final dosage of chemical required to achieve the desired result. For a 500 MW unit with a 10 000 Btu/kWh heat rate, the cost of CoalTreat is about $1.0 million/year.

This economic equation must be balanced with the revenue generated by fuel savings and a more efficiently operating unit. For example, a PRB unit treated with CoalTreat resulted in a decrease in furnace exit gas temperatures of 100°F. Given the rule of thumb that every 10°F decrease in furnace outlet temp results in a heat rate improvement of 0.25%, the unit average heat rate improved after CoalTreat by 2.5% or 250 Btu/kWh. At $0.75/mmBtu for PRB and 70% capacity factor, the unit saves about $0.5 million/year in fuel purchases. Also, CoalTreat increased the maximum output of the plant by 10 MW. Power at this plant was sold for $50/MWh, thus the increase in revenue was approximately $3.0 million/yr. Annual net revenue for the plant increased by $2.5 million. Not included in this simple estimate are revenue losses incurred by forced outage hours, reduced capacity factor, lost on-peak power sales, or the additional labour and material costs associated with cleaning slagged furnace tubes as well as their impact on tube life.

Closing the loop

Correcting coal ash chemistry in real time is now possible. A CoalTreat SMART system was recently commissioned that receives iron and sulphur content signals from an on-line coal analyser to automatically adjust the chemical blend ratio and dosage of reagents as the coal is bunkered. The SMART system ensures the power plant operator only treats incoming coal when needed. This process also relieves the operator from manually blending coal deliveries in the coal yard to meet the fuel quality needs of the furnace.