Solutions
for **Severe** Corrosion

Linas Mazeika, President, 3L&T Inc., USA, reveals how to prevent equipment corrosion caused by hot combustion gases in a cement plant.

Summary

The serious economic consequences of corrosion damage in cement plants have become a problem of global significance. Industries that are energy intensive, such as cement, often experience severe corrosion damage caused by hot combustion gases. Baghouse filters, ESPs, ducts, fans and chimneys can experience corrosion rates in excess of 1 mm per year. Additionally, corrosion causes plant shutdowns, a waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance and expensive overdesign that can jeopardise safety. A number of methods attempting to prevent metal corrosion have been developed with limited success. Currently there are new material technologies available to solve this type of

corrosion depending on the temperature range of the corrosive gases. A proven hybrid organic-inorganic coating can protect the metal in the range of 140 – 225 °C. A new inorganic polymer material can be used to protect steel up to 425 °C. A recent material technology based on an interpenetrating polymeric system has been successfully used in the 100 – 255 °C range, mainly in corroding chimneys.

This article will focus on major issues regarding corrosion caused by hot acid gases, starting from the causes to the consequences, and concluding with prevention and control.

Introduction

The corrosion mechanism and its severity vary with the nature of the hot combustion gases and the atmosphere in which the corrosion takes place. There are four main factors that affect the severity of corrosion: low pH, high temperature, high moisture and abrasion.

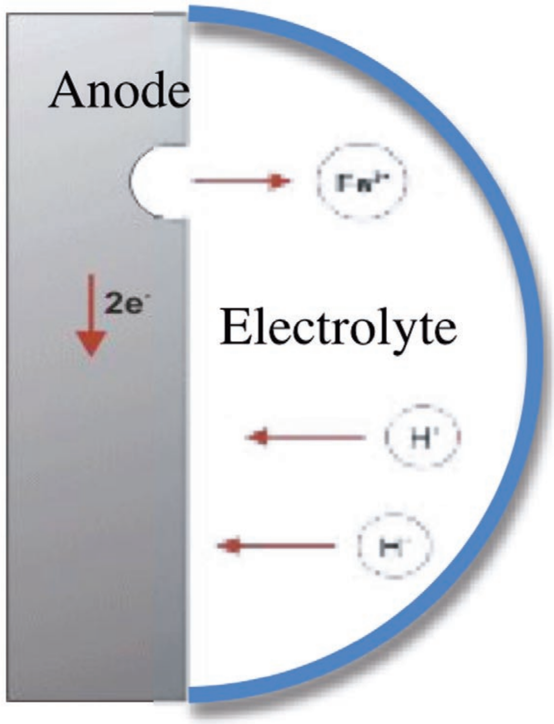

Figure 1. Schematic of metal electrochemical corrosion.

Figure 2. Severe corrosion damage in a reverse air baghouse filter.

Condensate pH values can be <1 and are the result of sulfur oxides, mainly SO_3, and chlorides produced during the combustion of fuels or calcination of raw materials. This acidic condensate will aggressively corrode carbon steel and even stainless steel, and is the main reason for the undercut failures of many coatings.

High temperatures will affect the integrity of polymeric coatings and fibreglass-reinforced plastics to the point of total failure. The effect on metals is usually the opposite. At temperatures above the dew point there is less corrosion, but there are environmental temperature limitations to reduce the emissions of dioxins and furans.

Higher moisture content increases the amount of condensation, and even small amounts of SO_3 in the range of 200 ppm will increase the dew point to above 150 °C. This means more areas are exposed to internal corrosion.

Abrasion mainly happens when the flyash impinges on dry areas of the system, removing the thin layer of rust and exposing the steel to corrosion. This creates an abrasion/corrosion vicious cycle.

Air pollution control devices, the fans and the stacks are all candidates for corrosion. Water spray cooling towers used to control temperatures amplify the problem. Some plants have acid gas scrubbers, which are also problematic if they are not protected. In these systems, the stack would also be a problem area. In general, most of the corrosion develops in equipment operating in the cooler end of the process. The corrosion in these areas can be worse with cold air leakage, low external temperatures, and frequent startups and shutdowns.

Corrosion process

Corrosion by hot acidic condensate is an electrolytic reaction involving an exchange of electrons and ions. It takes place between dissimilar areas of metal where there are differences in electrochemical potential. These occur naturally from the effects of oxides, impurities, alloy phases and metallurgy. Any corrosive situation requires a conducting electrolyte to establish the electrical circuit. A typical corrosion cell can be described as metal dissolving at the anode, while the electrons are consumed by a secondary process at the cathode and generate hydroxyl ions. The reaction between the dissolved metal and the hydroxide ions then generates the characteristic corrosion products.

With hot combustion gases, the acid condensate is the conductive electrolyte and the low pH increases its conductivity. The elevated temperature accelerates the metal attack on the anionic areas, and the particles in the gases remove the corrosion products from the surface and expose new metal to corrosion. This explains why in some areas the rate of metal loss can be higher than 1 mm per year.

Corrosion control

There are different methods that have been tried to reduce the corrosion impact. In some cases, operators attempt to maintain process gas temperatures above the dew point and/or remove corrosive gas constituents. Maintaining a high gas temperature to avoid condensation on the equipment walls can be expensive and in some cases limited by environmental regulations. This approach does not eliminate condensation during startup and shutdown, when temperatures rise

A proper understanding of process variables, raw materials and fuels is key to determining what type of materials to use to prevent corrosion.

Figure 3. ESP walls made of SS304, corroding severely.

Figure 4. Blistering and delamination of an epoxy coating.

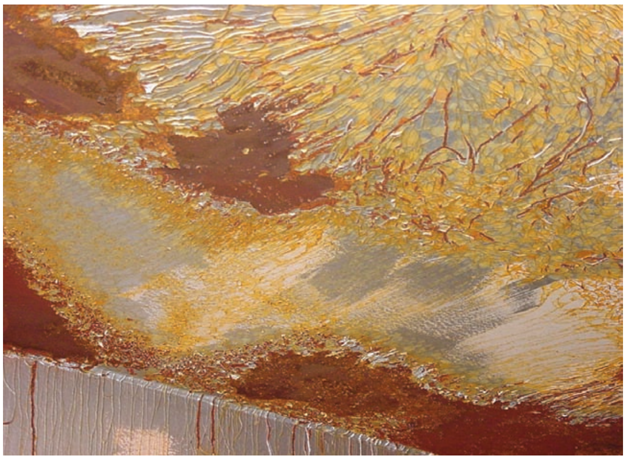

Figure 5. Catastrophic failure of a high temperature coating.

and fall through the dew point. Removing corrosive gas constituents requires scrubbing equipment, which adds to the capital investment and the operating cost.

Different construction materials, like 316L or higher alloys, can lead to 3 - 10 times higher capital investment and involves the risk of stress corrosion cracking.

Traditional coatings require an intensive surface preparation and multiple layers. This is expensive and they usually have a limited useful life due to blistering and delamination.

Thermal insulation

Proper insulation and its maintenance can sometimes reduce corrosion problems under the right conditions. However, insulated equipment with operating gas temperatures close to the dew point can still have significant corrosion. Figure 2 shows the inside of an insulated baghouse filter that has experienced severe corrosion. This baghouse operates in a high sulfur environment near the dew point. The walls are corroding and rust scale is falling on the tube sheet along the walls.

Corrosion-resistant metal alloys

Stainless steels are alloys of iron that generally have a minimum of 12% chromium. More chromium can be added to increase corrosion resistance. Alloys containing Molybdenum have improved resistance to pitting and crevice corrosion. The addition of nickel provides resistance to reducing environments. When nickel comprises more than 25% of the metal, it improves the stress corrosion cracking resistance. Figure 2 shows an ESP made of SS304. The chlorides present in the gases are corroding the walls badly.

If process gas temperatures operate at above 300 °C (570 °F), these materials are frequently a solution to corrosion. Equipment, ductwork, and stacks fabricated of these alloys, however, are very expensive - currently the cost of a 304 stainless steel is five times higher than carbon steel.

A proper understanding of process variables, raw materials, and fuels is key to determining what type of materials to use to prevent corrosion. Problems may arise when raw material, fuels, and temperatures are not as originally expected. Examples are alternative fuel utilisation, raw material substitution, or changing to high sulfur coal or petcoke.

Conventional protective coatings

Many coatings have been developed for severe corrosion protection. High-end, epoxy-based coating materials can resist the chemical attack of acid condensation to some degree; their high temperature performance is limited to ~150 °C in wet environments due to thermal degradation. The most common failure mode of organic coatings starts with blistering. This is followed by cracks and finally by corrosion under the exposed borders. Initially the oxygen is supplied through the coating layer and forms solid corrosion products. The length of the oxygen transport path to the interface at the edge of the blister is shorter than inside the blister where oxygen also has to diffuse through the corrosion products. The cathodic reaction will occur at the edge of the blister and the anodic reaction in the centre. The separation of the anodic and cathodic reaction sites is promoted by the nature of the corrosion products. When corrosion products are species that can be further oxidised,

Figure 6. Test plate retrieved after five months of exposure.

Figure 7. Corrosion stops right at the edge of the protective coating.

oxygen will be reduced during the transport through the corrosion products. In the case of carbon steel, the initial corrosion product is Fe^{2+}. In the presence of oxygen, it will be oxidised to Fe^{3+} and will consume the oxygen. The corrosion process leads to a film growth at the centre of the blister, which hinders further oxygen transport to that area. The growth of blisters under intact coating is due to cathodic delamination. Figure 4 illustrates this type of failure.

There are high temperature silicone coatings that can operate up to 500 °C in dry environments, but in hot combustion gas systems they tend to fail in a few months. Failure mode is filiform corrosion and delamination, as shown in Figure 5. For defective coatings, the corrosion process is more complex. Part of the metal substrate is exposed to the corrosive solution. The process starts with randomly distributed anodes and cathodes in the delaminated area. In the case of iron, Fe^{2+} is further oxidised to Fe^{3+} by oxygen and forms insoluble corrosion products, which can block that area and oxygen will penetrate in a weaker zone producing an anodic region. Propagation of corrosion depends on the nature of the corrosion products in the pore. The type of delamination will depend on the ratio of transport rates through the coating and through the formed corrosion products. When the rate of oxygen transport through the coating is higher, the mechanism is cathodic delamination; the opposite leads to anodic undermining.

New material technologies

3L&T has developed new material technologies for high temperature corrosion protection. Each of these new materials was initially intended to address a specific problem, and then the company found additional applications.

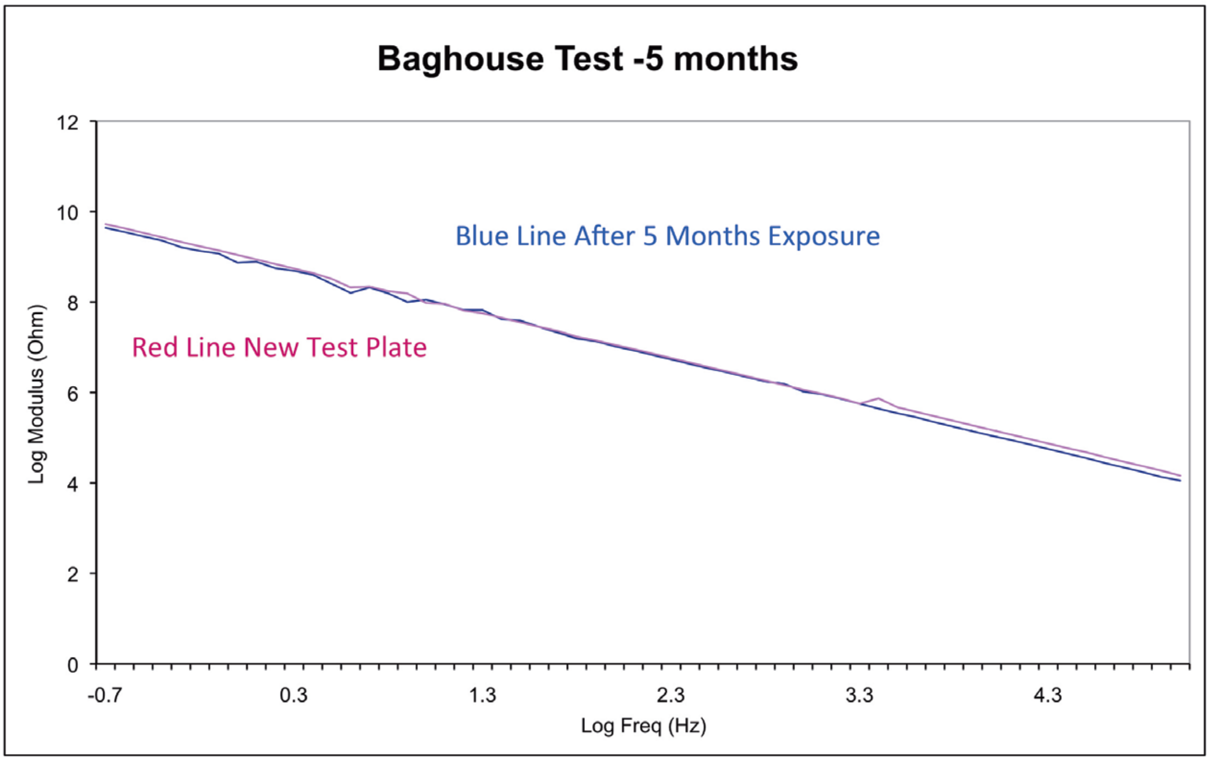

Figure 8. Electrochemical Impedance Spectra, before and after exposure.

The initial objective was to solve corrosion problems in cement plant dust removal equipment. The normal operating temperature range of the gases is 140 – 225 ˚C, with peaks up to 270 ˚C. The main cause of corrosion is the presence of SO_2 and SO_3 from sulfur in the fuel, and chlorides from alternative fuels or due to their proximity to the coast.

Figure 9. Inspection of FlueGard-225SQC after five years in a baghouse filter, showing no corrosion.

Figure 10. New baghouse filter coated with FlueGard-425S and cured at 200 ˚C.

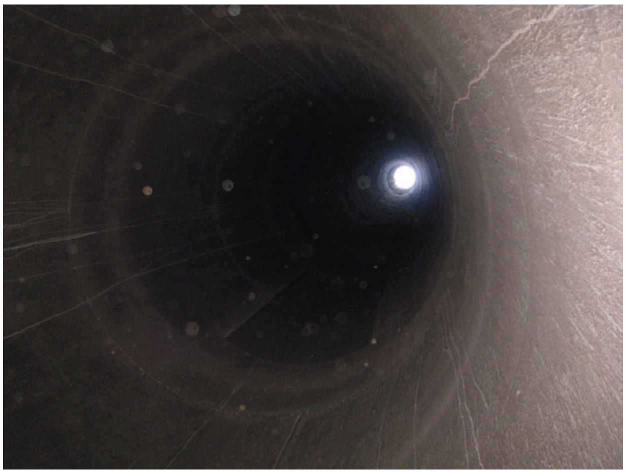

Figure 11. Large chimney coated with StackGard-255SQW, 15 months after application.

The main development target was to prevent blister formation under the coating. This was achieved using a very high cross-linked binder and a robust dry film thickness of 500 μm in a single layer. Additionally, the coating has to survive the expected operating temperature and this was achieved by the incorporation of several inorganic fillers.

To demonstrate the performance of the new material, 3L&T installed test plates inside the baghouse filter, exposing the coating to the actual operating conditions. The test plates were retrieved after several months in service for analysis. Figure 6 shows one sample as received.

After cleaning the test plate, the coating was in very good condition, the corrosion rate in the exposed metal border was measured at >1 mm per year. Most importantly, after cutting through the metal to expose a cross-section of the coating, it is clear that the corrosion stops right at the edge, i.e., there is no undercut corrosion. This can be observed in Figure 7. The reason for this unusual behaviour is the nature of the interface between the coating and the metal. The chemistry of the coating produces a passivation of the metal surface. This passivation prevents the formation of cathodic and anodic regions that are the drivers of the undercut corrosion.

The layer was tested in the laboratory using Electrochemical Impedance Spectroscopy (EIS). This is a modern technique available to characterise the electrical properties of organic coatings and their adhesion to metal surfaces. A coated test plate was measured before and after five months of exposure inside a baghouse filter. The two lines of the Bode plot in Figure 8 almost overlap, indicating that there is no measurable damage to the integrity of the coat.

Corrosion protection up to 225 ˚C

A cement plant in Oregon was looking for a solution to corrosion issues in its kiln baghouse filter. It was using high sulfur coal as fuel, and after only two years in service already had perforations in the walls.

3L&T installed a hybrid organic-inorganic polymeric alloy material, suitable for continuous operation up to 225 ˚C (437 ˚F) and which can handle peaks for several hours up to 270 ˚C (518 ˚F). This material, known as FlueGard-225SQC, has a tenacious bonding to steel and high resistance to hot acids and abrasion.

The first successful applications commenced more than six years ago, with numerous installations to date in different baghouse filters, ESPs, fans and ducts.

There are currently several ongoing projects in different industries like cement, lime, power generation, metal smelting, waste incineration, glass and battery recycling. Figure 9 shows the effectiveness of this corrosion protection system in a bag hose filter after five years in service.

This hybrid polymer-based coating technology is a robust solution to corrosion protection in flue gas treatment equipment. Additional R&D has further increased the performance and longevity of the equipment.

The coating material was initially used for maintenance, when actual conditions indicated excessive corrosion. Many users apply it during new equipment construction, before corrosion starts. A successful coating application requires proper surface preparation, correct application technique, and proper high temperature cure.

Corrosion protection up to 425 ˚C

This material was developed to address corrosion problems at very high temperatures. This new system is a combination of an inorganic polymer binder and two reactive inorganic fillers that have particle sizes in the nanometer range. The available surface of these fillers is about one million times larger than conventional materials and the end result is a corrosion protection coating that works well up to 425 ˚C and resists exposures up to 550 ˚C. Figure 10 shows a new baghouse filter coated with this material called FlueGard-425S. This project was for a cement plant in Mexico.

Corrosion protection in chimneys

The internal corrosion of chimneys is a pervasive problem in many industrial plants. It is difficult to address because there is usually a large temperature differential from the base to the top of the structure.

Many cement plant maintenance managers have expressed the need for better protection of steel chimneys and this has led 3L&T to develop a suitable material. The binder is an interpenetrating network made of organic and inorganic polymers. This produces a very densely cross-linked material with excellent thermal, mechanical and chemical resistance. The formulation includes multiple corrosion protection mechanisms that are effective within different temperature ranges. This is necessary because of the wide temperature difference that is common from the base to the top of most chimneys. Additionally, the StackGard-255SQW also has a wide temperature range for the final cure; from 100 to 180 ˚C. This is important because in most chimneys it is very difficult to heat the metal at the same temperature. Figure 11 shows a chimney coated over a year ago.

Conclusion

There are solutions to severe corrosion. Different corrosion issues in the plant may require different protective materials. If nothing is done, corrosion will add to the cost of maintenance, downtime, and efficiency. If the wrong solution is chosen, it will create additional maintenance costs.

Recognising the short and long-term economic impact of corrosion can rationalise the capital investment when selecting a cost-effective corrosion control solution. A good understanding of the operating conditions and determining suitable corrosion prevention methods increases the capital cost, but will lessen the subsequent maintenance, lost production, and the cost to run inefficient equipment.

Whether in new plants, plant expansions, or modifications, the need for corrosion prevention must be evaluated. Investing time and money up-front will save a lot of time, production and money over the operating life of the equipment. Corrosion, when understood, can be controlled with cost-effective solutions.

The key and often most difficult step is designing a corrosion protection mechanism.

A long-term performance coating must be able to survive the chemical attack, the operating temperature including any expected excursions, the fine particle abrasion and, most important, it must survive undercut corrosion in case of any local damage.