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Improving Thermocouple Service Life in Slagging Gasifiers

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Abstract

The measurement of temperature within slagging gasifiers for long periods of time is difficult/impossible because of sensor failure or blockage of inputs used to monitor gasifier temperature. One of the most common means of temperature measurement in a gasifier is physically, through the use of thermocouples in a gasifier sidewall. These units can fail during startup, standby, or during the first 40-90 days of gasifier service. Failure can be caused by a number of issues; including thermocouple design, construction, placement in the gasifier, gasifier operation, and molten slag attack of the materials used in a thermocouple assembly. Lack of temperature control in a gasifier can lead to improper preheating, slag buildup on gasifier sidewalls, slag attack of gasifier refractories used to line a gasifier, or changes in desired gas output from a gasifier. A general outline of thermocouple failure issues and attempts by the Albany Research Center to improve the service life of thermocouples will be discussed.

Introduction

Gasifiers are the heart of Integrated Gasification Combined Cycle (IGCC) power system currently being developed as part of the DOE's Advanced Fossil Fuel Power Plant. Gasifiers are also used to produce chemicals that serve as feedstock for other industrial processes, and are considered a potential source of H_2 in applications such as fuel cells. An IGCC gasification chamber is a high pressure/high temperature reaction vessel used to contain a mixture of O_2, H_2O, and coal (or other carbon-containing materials) while it is converted into thermal energy and chemicals (H_2, CO, and CH_4). In a slagging gasifier, the reaction chamber operates at temperatures between about 1250º-1550ºC, at pressures up to 1000 psi, and is lined with refractory materials to contain the severe environment and to protect the outer steel shell from erosion, corrosion, and temperature. An example of an IGCC gasification system with an air cooled slagging gasifier is shown in Figure 1. IGCC systems are expected to play a dominant role in meeting the Nation's future energy needs. A distinct advantage of gasifiers is their ability to meet or exceed current and anticipated future environmental emission regulations for combustion of coal of other carbon sources. Also, because gasification systems are part of a closed circuit, gasifiers are considered process ready to capture CO_2 emissions for reuse or processing should that become necessary or economically feasible in the future.

Slagging gasifiers have performance issues impacting IGCC economics, reliability, and on-line availability which have prevented them from being used more widely used by industry. A recent survey by twenty-two gasification industry stakeholders identified the improvement of gasifier instrumentation and control systems as the third most frequently cited research and development need [1]. Temperature measurement and control is critical during gasifier startup/cool down, during standby operation (in the case of a dual train gasification system), and during gasification. Two primary types of air cooled slagging gasifiers used in industry are shown in figure 2, each with similar temperature monitoring issues. These issues are traceable to severe service environments unique to the gasification industry that make reliable and continuous real time measurement of temperature in the gasification chamber difficult/impossible. These temperature monitoring issues include high temperature, oxidizing/reducing gases, particulate abrasion, and molten slag attack from ash in the carbon source.

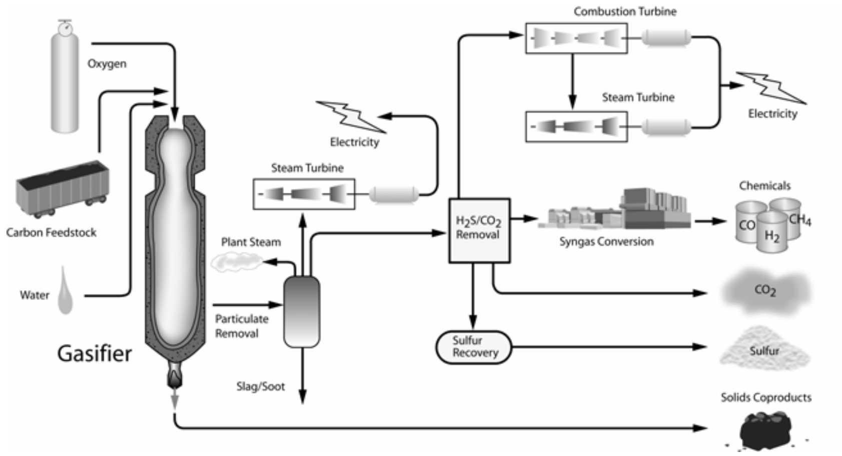


Figure 1: Integrated Gasification Combined Cycle gasification system.

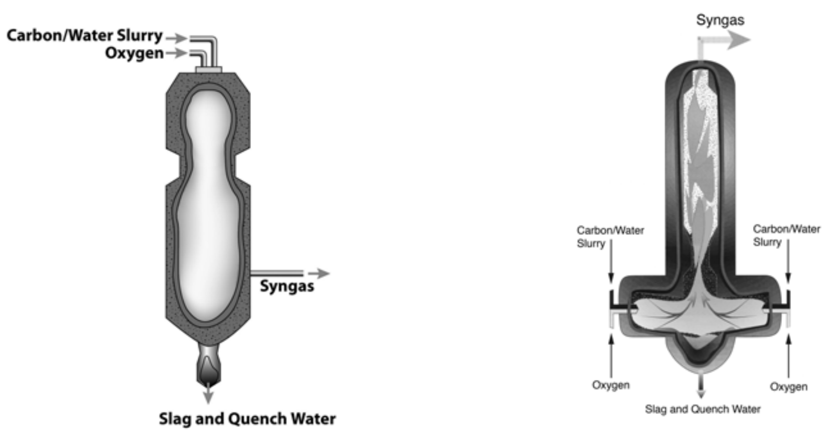


Figure 2 – Two types of air cooled slagging gasification chambers used in IGCC systems.

Traditional means of temperature monitoring in gasification chambers has been through the use of platinum-rhodium thermocouples, which create a thermal electromotive force (EMF) due to the Seebeck effect for joined dissimilar metals [2]. This low voltage electro-motive force (EMF) varies with temperature and is the basis for temperature monitoring in a gasifier. In their simplest form, a gasification thermocouple assembly is shown in figure 3, and is composed of a mounting flange that attaches it to the gasifier, two dissimilar wires joined at a tip where the temperature is measured, an outer protection tube, and a protective refractory ceramic cover. Because of corrosive molten slag, abrasion, temperature, hot gases, and other factors in a gasifier, the dissimilar wire in thermocouples requires an outer protection material. Depending on the thickness of the tube and of the refractory material added for additional protection, the response time to a change in gasification temperature varies, with increasing protection tube thickness or increasing refractory wall thickness creating greater response time lag. Historically, the evolution of refractory materials used to line and protect the high pressure steel reaction chamber has been towards high chrome oxide compositions, material which also forms the basis for filler material used to protect the thermocouple.

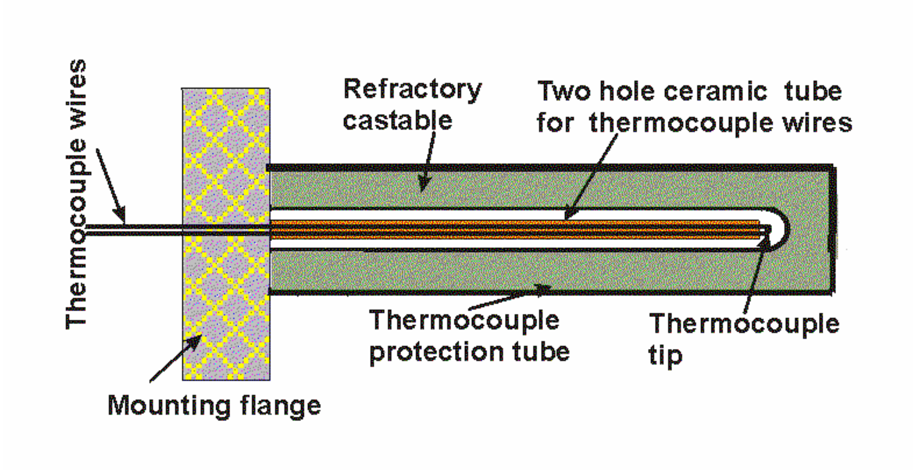


Figure 3. Basic gasification thermocouple assembly

The traditional thermocouple used to monitor temperature in a gasification chambers has a short service life, varying from failure during startup to about 45-90 days of service (longer in rare cases). After prolonged service, it is considered unusual for a thermocouples assembly to survive beyond one cycle (up/down gasifier cycle), when the thermocouple assembly is typically removed and replaced. Thermocouples are placed at various points in a gasifier, with each unit typically containing more than one thermocouples staggered at various depths, theoretically enabling the gasifier operator to monitor temperature as the refractory hot face (and the thermocouple hot face) gradually wears away.

Thermocouples fail in many ways, ranging from where no reading is produced (outright failure and an open circuit) to gradual drift or erratic readings. Because of the lack of reliability, other techniques have been and are being evaluated for use as backup to infer temperature measurement in the gasifier during operation. The most common type of alternative temperature measurement is through syngas analysis, where temperature is inferred from gas concentration (typically methane) during the gasifier operation, and is based on thermodynamic equilibrium calculations. This type of temperature measurement can only be utilized during gasification. It has a drawback in that the response time of gas concentration has a time lag that is too slow to detect rapid changes in the gasifier operation, and can lead to gasifier temperature changes impacting gasifier efficiency and product output, and can cause unnecessary refractory wear. The effect of higher temperatures on refractory wear is caused by slag dissolution of the refractory, which increases exponentially with temperatures increases [3], severely shortening refractory service life. Other effects from the lack of temperature control in a gasifier include improper preheating/cooling or slag buildup on gasifier sidewalls that can clog a gasifier or cause tear-out of refractory sections. Slag originates from ash in the carbon feedstock for gasification, and is present in different impurity quantities and chemistries in the coal or petroleum coke commonly used as a source of carbon. Each ash source has different corrosive behavior on thermocouple and refractory liner materials. Potential future sources of carbon, such as biomass waste or black liquor, will present new erosion and corrosion concerns in gasification.

When compared to the cost of repair or relining a gasifier, thermocouple replacement costs may seem minor (the cost of a replacement thermocouple is approximately $2,500 versus up to $1 million or more for a refractory lining), but the impact of a thermocouple on a gasifiers efficiency and service life is critical. In a USDOE sponsored report issued in 2001 [4], it was estimated that for every one pct improvement in efficiency gained from gasifier controls and sensor improvements (sensors include, but are not limited to thermocouples), a $409 million annual fuel savings would occur. It was also estimated that a one pct increase in gasifier availability in industry brought about through improved control and accurate sensing would result in a 5,000 MW of power increase without any additional gasification equipment.

A number of ways have been utilized or are possible to utilize in gasifier temperature monitoring, many of which were summarized in a workshop sponsored by US DOE's National Energy Technology Laboratory in 2001 [4], and which are summarized in table 1. Most ways listed in table 1 are not practical to utilize in gasifier temperature monitoring because of the high operating temperatures, oxidizing/reducing atmosphere sensitivity, slag corrosion issues, blocked optical paths, or gas composition sensitivity. Sapphire probe/fiber optics, for instance, are subject to high temperature issues such as corrosion or long term performance reliability problems; while techniques such as the infrared pyrometer [5] (widely used in the steel industry) are subject to slag and ash blockage of the viewing ports. Because of performance or technological limitations of many technologies listed in table 1, thermocouples are still the industrial standard, despite their listed shortcomings.

Table 1 – Potential Technologies for High Temperature Measurement [4]

Technology	Type	Comment
Thermocouple	Contact	● Thermocouples service extends to 2054^{o}C in benign atmosphere ● Wires limited to 1940^{o}C in inert atm, 650^{o}C in oxidizing atm ● Need sheaths that resist corrosion and erosion, ● Response times may be slow
Sapphire probe/ Fiber optics	Contact	● Can operate at temperatures of 2200^{o}C in a harsh atm. ● Issues include corrosion, vibration, performance near upper temperature limit, response in slag environment ● Commercially available up to 1200^{o}C in an oxidizing atm
Other contact technologies	Contact	● Resistive transmission, change, temperature detector - limit 650^{o}C ● Thin film thermocouples – Johnson noise
Two color infrared adsorption	Non-contact	● Gas path measurement performs well in clean gas atm with black body interference ● Used remotely in steel industry
Phosphor thermometry	Contact	● Point, imaging, and surface measurement ● Up to 1200^{o}C for surface measurement ● Current focus is to adapt technology for slagging gasifier – H_2S may poison phosphor material
Infrared pyrometer	Non-contact	● Potential to work up to 2480^{o}C
Time domain refractometer	Non-contact	● Uses a probe and has length limitation, tested to 1 meter
Gas-phase acoustic	Non-contact	● Low frequency, not sensitive to particulate; tested and used from 1200-1820^{o}C at atmospheric pressure ● Sensitive to types of gas but material in not a barrier ● Relating acoustic data to temperature is application specific
Other non-contact approaches	Non-contact	● FT/IR pyrometer, millimeter wave pyrometer, coherent anti-Stokes Raman scattering (CARS) system, and low-frequency pulse/broadband

ARC's program goal is to improve the reliability and service life of temperature measurement devices used in slagging gasifiers through materials research. This paper presents a general outline of thermocouple failure issues and early attempts by the Albany Research Center to improve the service life of thermocouples.

Thermocouple Failure Mechanisms

Thermocouple used to monitor temperature in a gasifier must go through the outer steel containment shell and through one or more layers of refractory liner materials as shown in figure 4. This refractory vessel is typically composed of a hot face or working lining (exposed to the slag, internal gasification temperature, particulate abrasion, and hot corrosive gases), a backup lining, and an insulating refractory material to lower the steel shell temperature. The thermocouple is bolted to the steel shell of the gasifier and forms a high pressure seal with the gasifier. The thermocouple is made of two dissimilar wires, typically platinum/platinum rhodium. These wires must go through the gasifier sidewall and again, have high pressure seals.

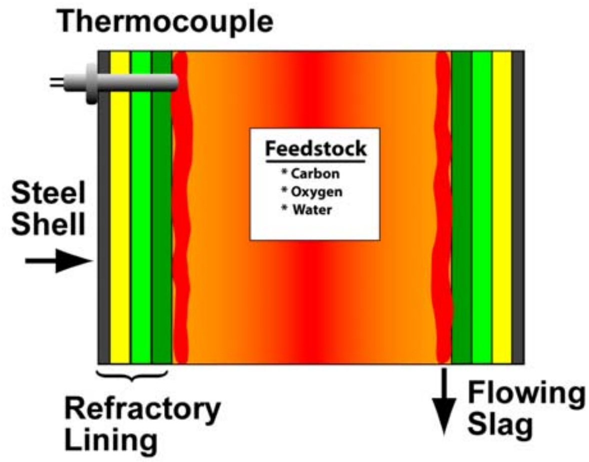


Figure 4 – Simplified drawing of thermocouple placement in an air cooled slagging gasifier.

Several of the possible causes leading to gasifier thermocouple failure are listed in the flowsheet of figure 5. These causes are based on observations made at gasifiers, discussions with gasifier users or fabricators, post-mortem analysis of thermocouples, discussions with thermocouple manufacturers, or originate from the root-cause analysis of possible causes of failure. Because of the expenses associated with shutting down a gasifier, obtaining a failed thermocouple when failure occurs is rarely done, making it difficult to know the real cause of thermocouple failure. It is also rare to obtain a thermocouple from a gasifier when it is shut down for repair, again making the determining thermocouple failure difficult. When thermocouple failure occurs during startup or preheat (before carbon feedstock is made into the gasifier), thermocouple assembly or installation defects are possible leading causes of failure. Once the gasifier is placed in gasification service (gasifier has a carbon feed), the determination of possible causes of failure is more difficult. Thermocouple failure during the first few days of gasification probably indicates a non-refractory issue. The possible causes of thermocouple failure (shown in figure 5) associated with the refractory are mechanical (strength), fabrication defects, or issues associated with chemical corrosion (slag, vapor, or metallic iron attack).

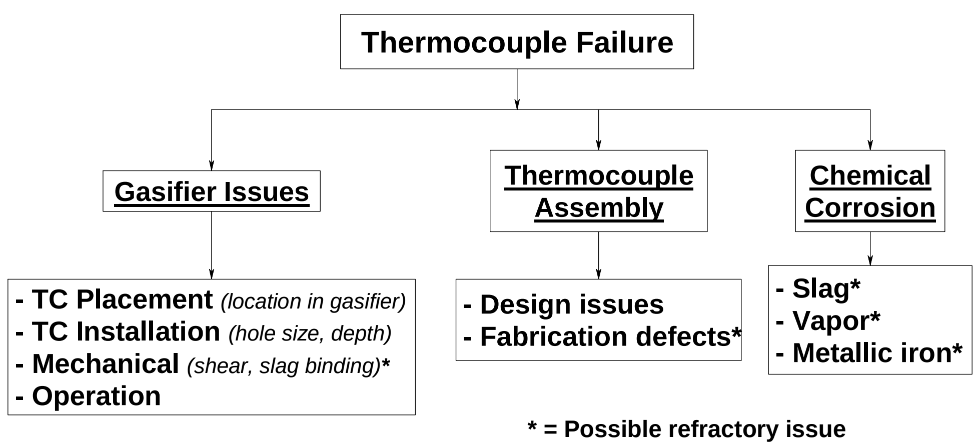


Figure 5 – Possible causes of thermocouple failure in a slagging IGCC gasifier

Gasifier Issues: Gasifier issues shown in figure 5 and causing thermocouple failure are under the control of the operator or are a consequence of the gasification process. They include where the thermocouple is placed (position in the gasifier and the angle of placement), how the thermocouple is installed (hole size and the depth a thermocouple is placed in relation to the refractory hot face), mechanical issues associated with gasifier refractory wall movement (shear or slag binding), and the how a gasifier is operated. When a thermocouple is installed in a new gasifier lining, the access hole for the thermocouple is aligned, permitting unimpeded thermocouple mounting. After use, however, differences in the thermal expansion behavior of the refractory linings create different amounts of lining movement, and set up a situation in a thermocouple where 1) binding and 2) shear can occur. An exaggeration of this refractory wall movement is shown in figure 6. During gasifier operation, another possible cause of thermocouple failure is created when slag will flows into the mounting hole, which becomes solid on gasifier shutdown. During gasifier operation, besides wall movement, slag can enter the thermocouple hole (shown in figure 6), which will solidify on cool down and remains attached to the refractory and to the thermocouple. The fixed thermocouple mounting bracket and the solid slag attached to the thermocouple and the hot face of the refractory do not allow dissimilar movement. Stresses can build up in the thermocouple with continued thermal cycling that can lead to thermocouple breakage when they exceed material strength. A thermocouple that has broken from shear or slag binding is shown in figure 7. Note that slag has penetrated the thermocouple hole and was penetrating into the back side of the thermocouple, allowing attack from behind the refractory barrier. Changing the angle of thermocouple entry may minimize some of these factors by reducing the amount of slag that can flow into hole and that may build-up at the hot face of the thermocouple. If vapor attack is a factor in thermocouple failure, techniques to stop vapor penetration in the thermocouple mounting hole or in the thermocouple itself must be developed.

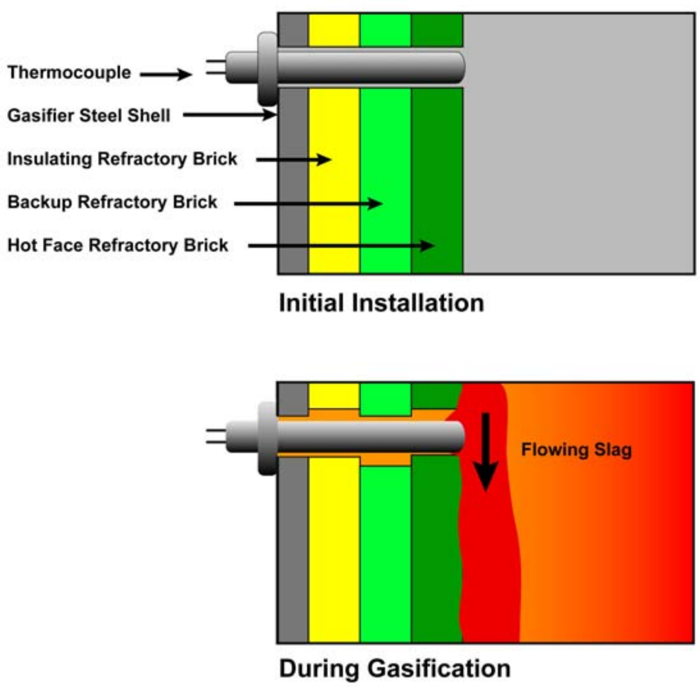


Figure 6 – Thermocouple installation in a gasifier that can lead to shear and slag binding during use, causing thermocouple failure.

Figure 7 – Failed thermocouple in a gasifier thermocouple port due to shear or slag binding. (Note that slag has infiltrated into the point where the thermocouple failed at the back side of the thermocouple.)

The operation of a gasifier is tied to the overall system design and operational variables. This can include variables such issues as gasification temperature, thermal cycling, material throughput, the amount and type of carbon feedstock, and ash chemistry. Most issues tied in with carbon feedstock end up determining the temperature of gasifier operation, the amount of slag throughput, the corrosive nature of the slag, and if additives are necessary or are made. All can impact thermocouple service life.

Thermocouple Assembly Issues: Thermocouple assembly issues shown in figure 5 are associated with thermocouple design or fabrication defects. A number of different designs have been evaluated as protective barriers for thermocouples to allow for the movement of the thermocouple and to protect the thermocouple sensing tip. The use of universal joints or flexible connectors between the front (temperature sensing end) and the mounting flange has allowed for some refractory wall movement. Elaborate designs have also attempted to extend thermocouple life through positioning in a gasifier, tapered refractory protective materials, coatings, different refractory fillers, or different protective tubes. Different refractory filler materials have been evaluated because they can vary in their ability to provide corrosion resistance and mechanical strength. Typically high chrome oxide refractory materials are used because they have proven themselves to be resistant to coal and petroleum coal slag attack. Different materials, however, may need to be utilized in the future based on possible changes in carbon feedstock. Fabrication defects can be present in thermocouple refractory filler material, and can include cracks, voids, or areas of varying bond strength. Refractory flaws may be created during thermocouple manufacture or processing, and could become avenues of slag or vapor attack of the thermocouple. Failure analysis should consider these factors. No single thermocouple design has proved satisfactory at all gasifiers.

Chemical Corrosion Issues: Chemical corrosion shown is figure 5 is thought to be the greatest cause of thermocouple failure in a gasifier, and can be associated with slag attack, vapor attack, or metal interactions. Corrosive issues can impact both the refractory filler and the protection tube, and may also interact with thermocouple wires. Ash in the carbon feedstock becomes molten at the elevated gasification temperatures, flowing down the refractory lining as shown in figure 4, causing slag corrosion by chemical dissolution. Because slag is constantly flowing over the refractory material, it never reaches static equilibrium, constantly corroding/eroding the lining. The ability of a material to resist corrosion is highly dependent on material interactions predicted by phase diagrams and thermodynamic reactions, with reaction kinetics also playing a role in material stability. Efforts are underway at the Albany Research Center to develop improved performance high chrome oxide or non-chrome oxide refratory filler.

Vapor from the gasification process or associated with the carbon feedstock may also attack the refractory lining, the thermocouple protection tube, or the thermocouple wires; any of which could lead to thermocouple failure. Vapor can be in the form of H_2S, CO, SO_x, or other gaseous species that may be present in the gasifier; and can condense or react directly with a material to form a new compound. Because vapor can penetrate pores, joints, or cracks in the refractory to a much greater depth than slag; reactions can occur in remote locations. A vapor like SO_x can also condense, creating a liquid that can cause liquid-solid corrosion. Thermodynamic stability, phase equilibrium, diffusion rates, and reaction rates are important aspects of the gasifier to consider before placing any material into service. It may be necessary to develop barriers to gaseous corrosion if this is a factor in thermocouple failure.

Metallic interactions leading to thermocouple failure occur when contaminants such as metallic iron or FeO (reacts with C to form CO and metallic Fe) are present in the slag. If contaminants such as Fe contact a thermocouple, they can change the chemistry and crystalline makeup of the Pt/Pt-Rh thermocouple wire, altering the EMP output, and thus the indicated temperature of the gasifier. It is also possible that components could also alter the wire composition enough to change the wire melting point, possibly to the point of melting or vaporizing material. Metallic Fe, for example, can reduce the melting point and alter the crystal structure of the Pt or Rh in thermocouples; while S can interact with Pt or Rh, possibly creating new phases as low as 444^{o}C [6].

Thermocouple Interactions

The gasifier environment can interact with a thermocouple in many ways, altering the EMF output. These interactions can be in the form of a resistance short across the thermocouple wires, or outright corrosion of the thermocouple wires, resulting in an electrically incomplete EMF circuits as shown in table 2. The resistive effect of the contact with carbon, slag, metal, or the gasifier environment is shown in figure 8.

Table 2 – Possible gasifier environment interactions with thermocouples

Reactant	Effect on the thermocouple
Slag	- Slag contact with the thermocouple wires may alter the EMF output by acting as a resistive bridge - Slag may corrode the thermocouple wires, breaking or altering the EMF output by acting as a resistive bridge
Metal	- Metallic iron in the slag may cause an electrical short or alter the EMF output by acting as a resistive bridge
Vapor	- Vapor or vapor condensation may cause a resistive short or a new phase to form, altering the EMF output by acting as a resistive bridge - Vapor may react with the thermocouple wire, breaking or altering the EMF output, acting as a resistive bridge
Carbon dust	- Buildup across the thermocouple wires can alter the EMF output by acting as a resistive bridge

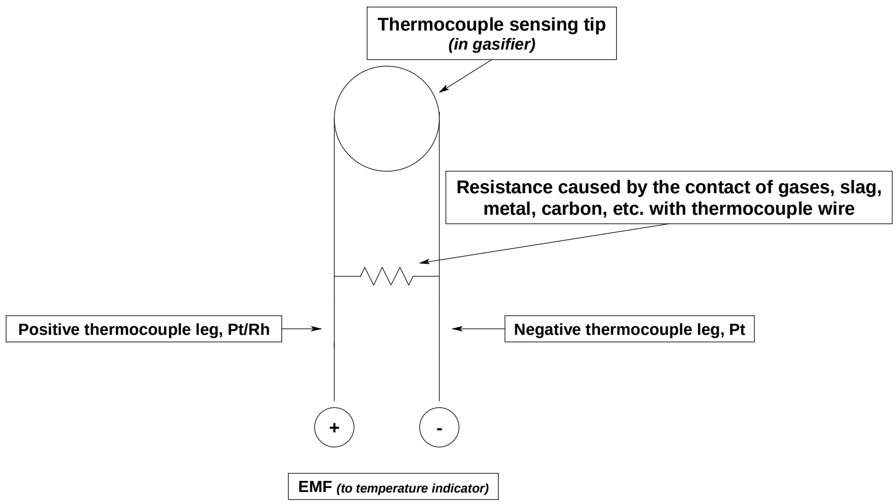
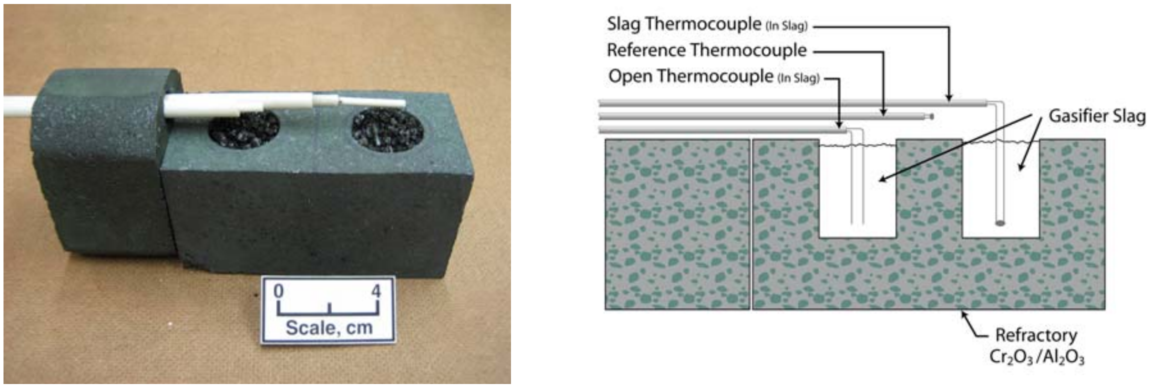


Figure 8 – Thermocouple used in gasifier environments

An evaluation of the attack of a gasifier slag on thermocouple wire is shown in figure 9 (a), where three types of type S thermocouples (Pt/Pt-10 pct Rh) were inserted above and into pulverized gasifier slag. This test was designed to indicate the effect of molten gasifier slag on thermocouple output. Two thermocouples were inserted in the slag, a welded thermocouple tip and an open thermocouple (no wire connection). The third thermocouple was an open reference above the crucible. A cross section of the test assembly is shown in figure 9 (b). The containment crucible was made of 90 pct Cr_2O_3/10 pct Al_2O_3, and was heated at a rate of 150°C/hr in an Ar environment to the indicated test temperature (measured at 1390°C), at which point the unit was held at temperature for approximately 3 hours. No thermocouple protection was used within the furnace. During the test, EMF was recorded versus time to give an indication what was occurring with the EMF output. EMF values above about 1600°C and below about 0°C are not indicative of real temperature. The EMF output from the thermocouples was recorded and plotted versus time (with temperature indicated on the second axis) and is shown on figure 10. It is of interest to the following items in figure 10:

1. The slag thermocouple and the reference thermocouple indicated the same temperature during heat-up until the slag thermocouple failed at about 880°C. (note that slag should not be molten at this temperature)
2. The open thermocouple in the slag indicated no real temperature for approximately 3.5 hours of the heat-up, at which time it began to indicate sporadic temperature measurements.
3. The reference thermocouple above the slag failed at 1400°C after approximately 2 hours of hold, after which it gave sporadic temperature readings. The reference thermocouple had no slag contact.
4. Thermocouple wires in the open system were completely removed where openly exposed to the gas environment in the test chamber, regardless of if they had slag contact or not. This indicated a possible vapor interaction with the Pt and Rh thermocouple wires.



a b

Figure 9: Type “S” thermocouple EMF output research showing (a) experimental setup and (b) a cross-section schematic of the setup. Three types of thermocouples are shown: 1) reference thermocouple with welded tip placed above the slag container, 2) welded thermocouple tip placed in gasifier slag, and 3) open thermocouple tip (not joined) placed in gasifier slag.

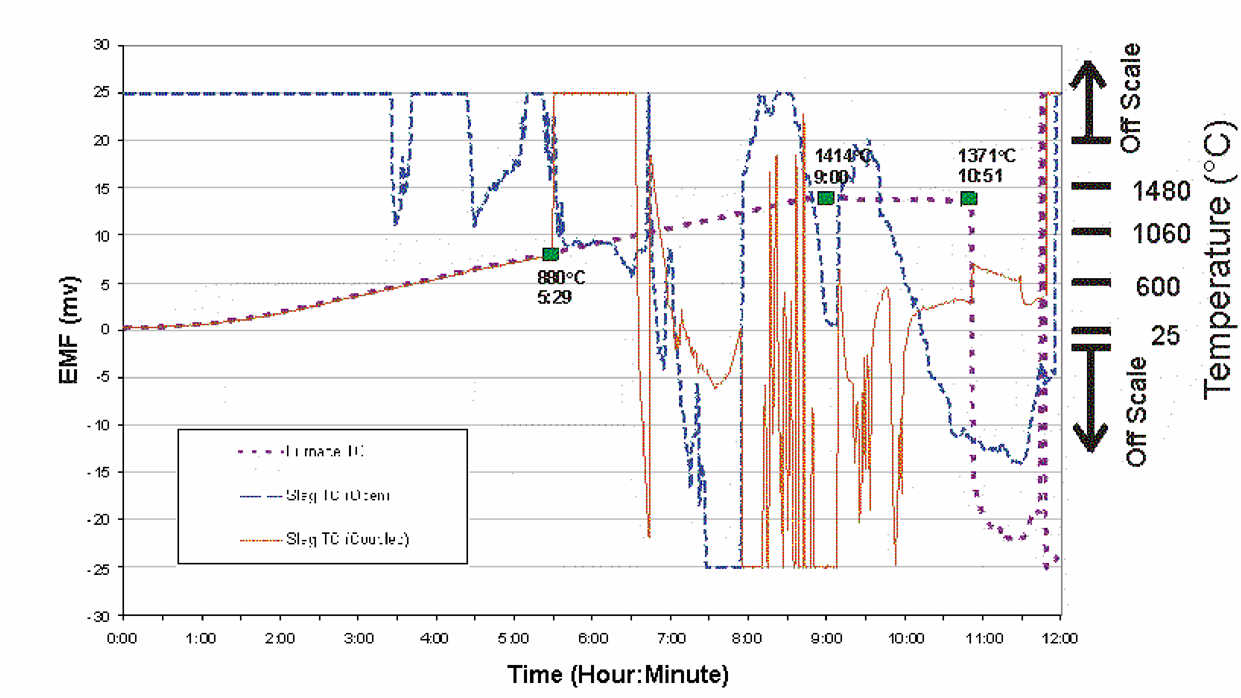


Figure 10. EMF output from type “S’ thermocouple tips heated in Ar to approximately 1400°C for 3 hours using a commercial gasifier slag.

The thermocouple test showed similar EMF output seen as failure when in commercial service. The EMF output that discontinued for slag exposed and atmosphere exposed thermocouples indicated a possible vapor attack of the thermocouples, and indicated that factors other slag or metal may play a role in thermocouple failure. It is not clear what role slag played in thermocouple EMF output. It is important to keep in mind that laboratory testing in a simulated gasifier environment may have differences from a commercial gasifier. Thermocouple failure may be caused by a combination of factors, many of which may be unique to a specific gasifier operation.

The Albany Research Center is working with different gasifier users, refractory manufacturers, and manufactures of gasifiers and thermocouples to improve thermocouple service life and reliability. A number of complex issues associated with the use of traditional thermocouples may lead to the failure, issues which may be unique to a specific user site or gasifier type. Performance issues also exist with alternative temperature measurement techniques, and are why they are not widely used in gasifiers. Greater study of these non-traditional temperature measurement techniques may be necessary, although more research is necessary to determine the cause of temperature monitoring failure and to determine if technology exists to overcome these causes. Reliable temperature monitoring systems of the future may utilize several techniques to monitor temperature, especially during heat up, cool down, or gasification.

Conclusion

Gasifiers are the heart of Integrated Gasification Combined Cycle (IGCC) power system currently being developed as part of the DOE's Advanced Fossil Fuel Power Plant. They can produce chemicals that serve as feedstock for other industrial processes, and are considered a potential source of H_2 in applications such as fuel cells. Slagging gasifiers have performance issues impacting IGCC economics, reliability, and on-line availability which have prevented them from being used more widely used by industry. The improvement of gasifier instrumentation and control technology has been identified as a critical research need. Temperature measurement and control is critical during gasifier startup/cool down, during standby operation (in the case of a dual train gasification system), and during gasification. Lack of temperature control in a gasifier can lead to improper operation, increased slag buildup on gasifier sidewalls, increased slag attack of gasifier refractories used to line a gasifier, or changes in desired gas output. A number of means exist for monitoring the temperature in a gasifier, but all suffer from performance issues including short service life, ash buildup, and corrosion. Thermocouples are the most widely used means of temperature measurement, but can fail during startup or within the first 45-90 days of gasification. The Albany Research Center is investigating ways to improve the reliability and service life of temperature measurement devices in gasifiers. The main failure mechanisms in thermocouples have been identified and include gasifier issues, thermocouple assembly issues, and corrosion attack. Different failure mechanisms may occur at different production facilities. Because removing a thermocouple assembly disrupts gasifier production, obtaining thermocouples once failure occurs is rare, making post-mortem analysis of the causes of failure difficult. For reliable temperature measurement in a gasifier, it may be necessary for gasifier users to measure temperature by more than on means. Hands-on research by Albany at several gasifier operations is focused on thermocouple assemblies to improve thermocouple performance.

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