Evaluation of different alternatives for increasing the reaction furnace temperature of Claus SRU by chemical equilibrium calculations

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Abstract

Application of different alternatives for increasing the reaction furnace temperature of Claus sulfur recovery units (SRUs) are investigated by chemical equilibrium calculations. The Gibbs free minimization method based on Lagrangian multipliers is used for formulating the problem. The usefulness of different techniques such as fuel gas spiking, indirect air and/or acid gas preheating, oxygen enrichment, acid gas enrichment and direct air preheating for increasing the furnace temperature are determined by the proposed algorithm. In the case of lean feed acid gases, it may be necessary to use a combination of methods in order to attain the minimum furnace temperature required for flame stability and complete destruction of acid gas hydrocarbon contaminants. It is found that the acid gas enrichment is a reliable technique for providing the required reaction furnace temperature when a high flow of too lean acid gas is to be processed in a Claus unit. The predicted reaction furnace temperatures are in good agreement with the measured experimental values.
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Keywords: Claus; Reaction; Furnace; SRU; Temperature

1. Introduction

The Claus process continues to be the most widely used process worldwide for the production of elemental sulfur from gaseous hydrogen sulfide [1]. The requirements to be met by Claus plants are dictated by the operating conditions of modern refineries and natural gas plants and increasingly stringent emission control regulations.

Several variations of the basic Claus process have been developed to handle a wide range of feed gas compositions [1,7,12]. Straight-through operation results in the highest overall sulfur recovery efficiency and is chosen whenever feasible. Air is supplied by blower and the combustion is carried out at 1–2 bar, depending on whether or not a tail gas treatment unit is installed downstream of the Claus plant.

In the modified Claus process, the overall reaction is separated into (1) a highly exothermic thermal or combus-tion reaction section (reaction furnace) in which most of the overall heat of reaction is released. (2) a moderately exothermic catalytic reaction section in which sulfur dioxide formed in the combustion section reacts with unburnt H_2S to form elemental sulfur [1,5].

The principal reactions taking place in the reaction furnace (Fig. 1) are [4,7]:

1. Oxidation of 1/3 of the H_2S in the feed to form SO_2. This reaction is highly exothermic and causes to increase the reaction furnace temperature and flame stability:

$$H_2S + \frac{3}{2}O_2 = SO_2 + H_2O \qquad (a)$$

2. A part of the sulfur dioxide (SO_2) formed in the reaction furnace, reacts with unburnt H_2S to form elemental sulfur. This endothermic reaction causes approximately $\frac{2}{3}$ of the total sulfur production:

$$2H_2S + SO_2 = \frac{3}{2}S_2 + 2H_2O \qquad (b)$$
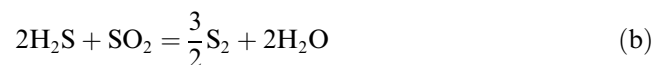
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Nomenclature

$a_{i,j}$	number of atoms of element i in one molecule of species j	NE	total number of elements in the system
b_i	number of moles of element i in the system	N_j	number of moles of species j
C_p	constant pressure specific heat	N_R	number of moles of reactant species
F	objective function defined in Eq. (1)	NS	total number of species
G	Gibbs free energy	P	system pressure
$\Delta G_{f,j}^{\circ}$	standard Gibbs energy change of formation for species j	$P_{\circ}$	reference pressure (=1 bar)
h_f°	enthalpy of formation of a species at 298 K and 0.1 MPa	R	gas constant
		T	reaction furnace temperature
		Δ	difference
N	total number of moles of species in the reaction mixture	ψ_i	dimensionless parameter defined in Eq. (8)
		μ_j	chemical potential of species j
		λ_i	Lagrangian parameter for element i

3. Combustion of hydrocarbons and other combustible contaminants. Because H_2S and SO_2 react in a 2:1 ratio, it is desirable to oxidize only one-third of the incoming H_2S.

This is a simplified interpretation of the reactions actually taking place in the reaction furnace. The reaction equilibrium is complicated by the existence of various species, whose equilibrium concentrations in relation to each other are not precisely known for the entire range of process conditions. Furthermore, side reactions involving hydrocarbons and CO_2 present in the acid gas feed can result in the formation of carbonyl sulfide (COS), carbon disulfide (CS_2), and carbon monoxide (CO) in the front-end furnace [1,5,6]. Therefore, the accurate prediction of furnace flame temperature and species concentrations are difficult tasks.

In this paper, we present a general formulation for determination of Claus reaction furnace temperature, equilibrium compositions and optimum air rate by Gibbs free energy minimization method [9]. Since some plants suffer from relatively low furnace temperature (usually due to low acid gas H_2S content) and have problems with efficiently destroying acid gas contaminants, the effectiveness of several commercially viable methods used for increasing the Claus furnace temperature are evaluated by the pro-

posed approach and the predicted results are compared with field experimental data.

2. Modeling

The Gibbs free energy of a system consisting of N species can be written [9]:

$$G = \sum_{j=1}^{NS} N_j \mu_j, \tag{1}$$

where μ_j is the chemical potential of species j in the reaction mixture. we wish to find out the set of mole numbers N_j's, which produces a minimum in G, however all the mole numbers are not independent because elemental balance constraints must also be satisfied. We have written these constraints as

$$\sum_{j=1}^{NS} a_{i,j} N_j - b_i = 0. \tag{2}$$

Here, b_i is the number of moles of element i in the system, $a_{i,j}$ is number of atoms of element i in one molecule of species j and NS is the total number of species. There will be one of these equations for each element ($i = 1, 2, \ldots NE$), where NE is the total number of elements in the system.
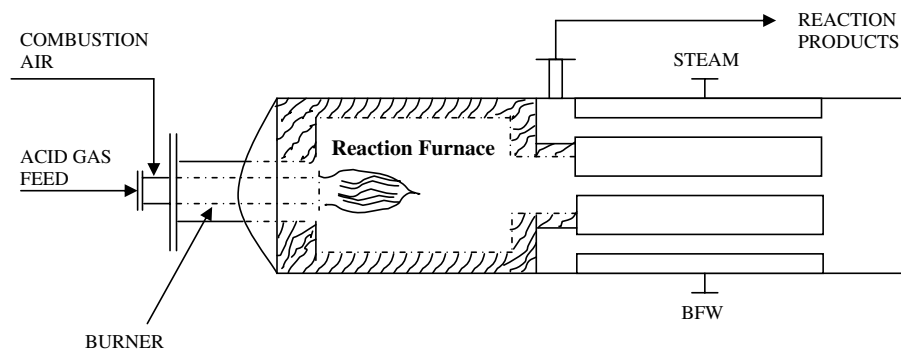

Fig. 1. Typical reaction furnace and waste heat boiler.

Introducing Lagrangian multipliers λ_i's, the objective function F can be written by Using Eqs. (1) and (2):

$$F = G + \sum_{i=1}^{NE} \lambda_i \left[\sum_{j=1}^{NS} a_{i,j} N_j - b_i \right] \tag{3}$$

The conditions for a minimum are determined by obtaining the partial derivatives of F with respect to N_j and setting them equal to zero. These results in

$$\mu_j + \sum_{i=1}^{NE} \lambda_i a_{i,j} = 0 \tag{4}$$

Since the operating pressure of Claus Reaction furnace is 1–2 bar, the gas mixture can be assumed to be perfect. Thus, the chemical potential of a species is given by

$$\mu_j = \Delta G_{f_j}^\circ + RT \ln \frac{P}{P_\circ} + RT \ln N_j - RT \ln N, \tag{5}$$

where $\Delta G_{f_j}^\circ$ is the standard Gibbs energy change of formation for species j [2,10], $P_\circ$ is 1 bar and P is system pressure. Combination with Eq. (4) gives

$$\frac{\Delta G_{f_j}^\circ}{RT} + \ln \frac{P}{P_\circ} + \ln N_j - \ln N + \sum_{i=1}^{NE} \frac{\lambda_i a_{i,j}}{RT} = 0 \tag{6}$$

This gives a system of "NS" equations, one for each species.

Finally, we have the condition that the total number of moles in the system must equal the sum of the individual mole numbers

$$\sum_{j=1}^{NS} N_j - N = 0 \tag{7}$$

Eqs. (2), (6) and (7) form a system of $NS + NE + 1$ equations. Since there are also $NS + NE + 1$ variables, the solution of the problem can be obtained.

In order to solve the problem, the Newton–Raphson method is used for simultaneous solution of Eqs. (2), (6) and (7). The system of equations can be written by choosing non-linear correction variables. These are $\Delta \ln N_j$, $\Delta \ln N$, and $\psi_i = -(\lambda_i / RT)$. Thus we have:

$$\Delta \ln N_j - \Delta \ln N - \sum_{i=1}^{NE} a_{i,j} \psi_i = -\frac{\mu_j}{RT} \tag{8}$$

$$\sum_{j=1}^{NS} a_{i,j} N_j \Delta \ln N_j = b_i - \sum_{j=1}^{NS} a_{i,j} N_j \tag{9}$$

$$\sum_{j=1}^{NS} N_j \Delta \ln N_j - N \Delta \ln N = N - \sum_{j=1}^{NS} N_j \tag{10}$$

Eqs. (8)–(10) can be collected together into a matrix format.

To start the solution, it is first necessary to specify the species likely to be present in significant amount at equilibrium. Since in the gas sweetening plants, the produced acid gas usually contain H_2S, CO_2, H_2O and light hydrocarbon contaminants, the reaction mixture is assumed here to contain 10 species namely, H_2S, CO_2, CO, SO_2, COS, CS_2, S_2, H_2, N_2 and H_2O according to our experience.

The solution algorithm is summarized as follows:

1. Make initial guess (e.g. 800 °C) for T.
2. Assume the air flow rate (By changing b_i).
3. Calculate the μ_j from Eq. (5) (knowing P and T), solve the matrix format of Eqs. (8)–(10) for the correction factors (using initial estimates of N_j) and use the correction factors to get the improved values of N_j and N by using the following equations:

$$(\ln N_j)_{\text{new}} = (\ln N_j)_{\text{old}} + (\Delta \ln N_j) \tag{11}$$

$$(\ln N)_{\text{new}} = (\ln N)_{\text{old}} + (\Delta \ln N) \tag{12}$$

   It should be noted that ψ_i reset to zero for each iteration. The iteration continues until a converged solution is obtained.
4. If the $N_{H_2S} / N_{SO_2} \neq 2$, a new air rate is used and calculation are repeated from step 3.
5. If the N_{H_2S} / N_{SO_2} ratio $= 2$, the assumed temperature should be checked by the following energy balance equation [11]:

$$\sum_R N_R [h_f^\circ + \Delta h]_R - \sum_P N_j [h_f^\circ + \Delta h]_j = 0, \tag{13}$$

   where

$$\Delta h = \int_{298.15}^{T} C_p(T) \mathrm{d}T. \tag{14}$$

   Required thermodynamic properties are taken from [2,8,10]. If the assumed temperature does not satisfy the above equation, a new T is assumed and the calculations are repeated from step 1.
6. If Eq. (13) is satisfied, the solution for the problem is obtained.

3. Results and discussion

The primary role of the Claus reaction furnace is to partially oxidize the H_2S in the acid gas feed to SO_2 and it will also produce a significant portion of the total sulfur product. A secondary role of the reaction furnace is to ensure destruction of the many contaminants in the acid gas feed stream. This will ensure that these compounds do not breakthrough to the downstream process units, where they can have a significant detrimental effect on the Claus catalyst activity. Therefore, it is critical to understand the relationship between various furnace operating parameters and the reaction furnace temperature.

There are different techniques to increase the furnace temperature, namely, fuel gas spiking, indirect air and/or acid gas preheating, oxygen enrichment, acid gas enrichment and direct air preheating [1,5,7]. The usefulness of each of these methods in increasing the furnace temperatures is investigated by the proposed algorithm and the

results are checked by plant experimental data. These are discussed in the following sections.

4. Fuel gas spiking

In this method [7], a plant fuel gas stream is added to the acid gas feed stream in the hope of substantially increasing the temperature of the furnace feed gas. Fig. 2 illustrates the effect of adding fuel gas to the reaction furnace for two different acid gas feeds (20 and 40 mol% H_2S) based on proposed model. These predicted results indicate that fuel gas spiking can result in significant temperature increase depending on the quality of the acid gas feed (from 30 to 50 °C per 1% equivalent fuel gas flow) as shown in Fig. 2. However, we can also see that fuel gas spiking is unlikely to raise the furnace temperature above the 1050 °C threshold [3–7] (recommended minimum temperature for flame stability and hydrocarbon dissociation) even for a 40% H_2S feed gas. Thus, there might be significant plant performance penalty to be paid due to the very large increase in CS_2 formation due to the higher hydrocarbon content of the combined feeds. The higher content of hydrocarbons also modifies the air content necessary to burn the H_2S, beyond the increase in secondary reactions with CS_2 formation.

Therefore, it would not normally be recommended to use a fuel gas spiking technique in order to increase the furnace temperature in an effort to ensure no hydrocarbon breakthrough from the furnace. Only in cases where the existing furnace temperature is very close to the threshold temperature would fuel gas spiking potentially result in the desired outcome. The predicted furnace temperatures are in good agreement with the plant data as shown in Fig. 2.

5. Indirect air and acid gas preheat

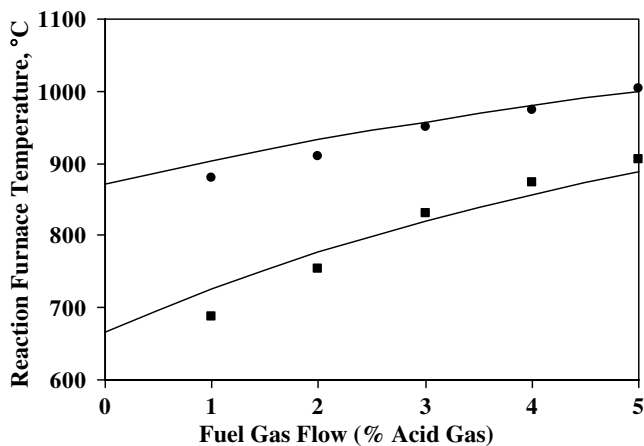Additional energy can be directly introduced into the reaction furnace by increasing the temperature of the air

Fig. 2. Effect of fuel gas spiking on reaction furnace temperature (-model prediction, experimental data: ■ 20% H_2S, ● 40% H_2S).
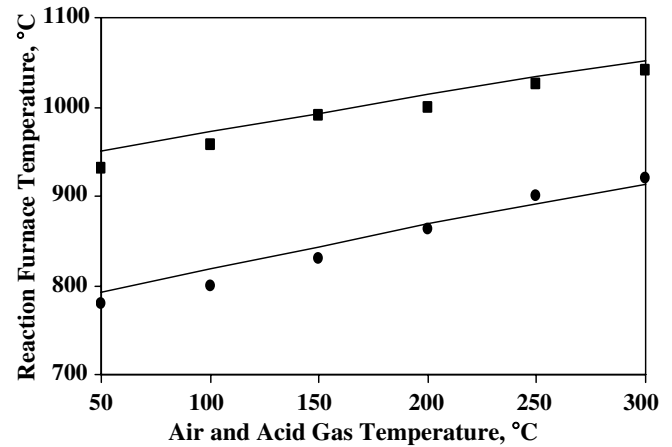

Fig. 3. Effect of preheating on reaction furnace temperature (-model prediction, experimental data: ● 30% H_2S, ■ 40% H_2S).

and/or acid gas feed streams [1,7]. This is commonly done in some ammonia destruction furnace schemes and has been used in some lean feed acid gas cases. The air and acid gas streams are usually preheated in an indirect heat exchanger system and the energy is provided by an external utility source. One of the primary disadvantage of this type of scheme is that the total amount of practical preheat which can be made available is somewhat limited. The first concern is that the acid gas and air delivery piping is normally carbon steel and is therefore limited to a maximum operating temperature of 300–350 °C. Also, the source of the input energy is often an existing steam utility system. Therefore, the source steam pressure has a direct effect on the maximum amount of preheat available. For 700 kPa steam, the maximum preheat temperature is approximately 240 °C.

Fig. 3 illustrates the potential impact of this range of preheat on the reaction furnace temperature for several acid gas cases. The temperature range chosen for this graph is consistent with the potential delivery temperature of 4100 kPa steam.

Using preheat has a direct and clear effect on the furnace temperature as shown in Fig. 3. The simulated results compared well with measured field data as shown in this Figure. However, for the range of preheat which is available, the increase in furnace temperature still falls below the desired threshold temperature of 1050 °C for all, but the 50% H_2S case. Therefore, while the increase in achievable temperature is significant, it may not ensure complete hydrocarbon destruction for many of the acid gas feed cases.

6. Direct fuel gas preheat burner

A relatively new process concept has been employed at small number of plants to improve the furnace temperature [6,7]. In this system, a fuel gas stream is utilized to add energy directly to the furnace system. However, instead of injecting the fuel gas directly into the furnace to be
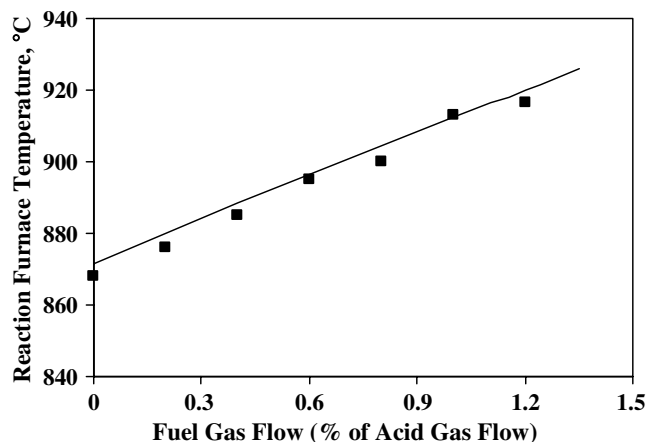
Fig. 4. Effect of direct fired preheat on reaction furnace temperature (-model prediction, experimental data: ■ 40% H_2S).

Fig. 5. Effect of oxygen enrichment on reaction furnace temperature (-model prediction, experimental data: ● 30% H_2S, ▲ 50% H_2S).

consumed in the furnace flame, the fuel gas is pre-burned in a dedicated burner to directly heat the combustion air stream. The fuel gas is pre-burned with an excess of air to ensure complete oxidation of the fuel gas. The combustion gas products (CO_2 and H_2O) are then pre-mixed with the balance of the combustion air, prior to delivery to the existing furnace burner.

The mixing of the combustion gas products (CO_2 and H_2O) with the combustion air can increase the corrosion of the steel equipment, and decrease the sulfur production [13]. The water content in the acid gas load is very important to the process. It should be noted that an excess of water vapor inverts the direction of Claus reaction (Eq. (b)), leading to a decrease in sulfur production. H_2O may also react with SO_2 and SO_3 to produce sulfuric acid which is a corrosive medium to Claus downstream steel equipments (e.g. catalytic converters) operating at lower temperatures [13–15].

The advantage of this system over direct fuel gas spiking are that there is no significant contribution to CS_2 formation in the furnace. The disadvantage of this system is that there is a limited amount of preheat, which can be added as a result of limitations on the preheated air temperature by the metallurgy of the air delivery piping.

Fig. 4 illustrates the effect of this style of preheat on furnace temperature for a 40% H_2S case. The furnace temperature should increase approximately 40 °C utilizing a full 300 °C preheat temperature. Based on these results it is clear that this method would only be appropriate for a case where the 40 °C furnace increase is adequate. The predicted and measured reaction furnace temperatures suggests that in a case with acid gas at 40% or less, this level of preheat would not result in attaining the minimum target temperature of 1050 °C.

7. Oxygen enrichment

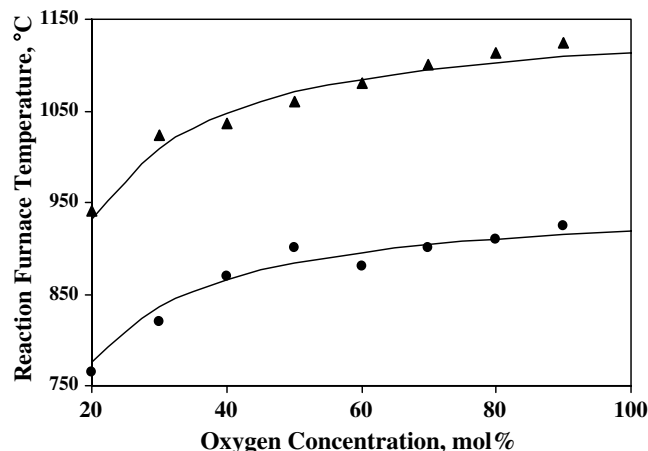Many plants are using oxygen enriched air streams in their SRUs for many reasons [3,5–7]. In most cases, oxygen

enrichment is used to increase the throughput capacity of the plant. However, in some specific cases, oxygen enrichment has been used to improve the furnace temperature. In some cases this has allowed for the processing of extremely lean acid gas and in others it has allowed for better overall furnace and burner operation.

The oxygen enrichment should be used with care. The precision control of the mixing of combustion gases is an essential factor in avoiding oxygen breakthrough into the downstream catalytic converters. The poor homogeneity in the combusting gases led to unreacted oxygen being available in the gas to further oxidize SO_2 to SO_3 either before the gas stream reached the catalyst bed or on the catalyst bed itself. This SO_3 then reacts with the alumina catalyst and deactivates it by forming aluminum sulfate. The SO_3 may also reacts with H_2O to produce sulfuric acid, which is a corrosive agent capable of damaging downstream steel equipments depending on variables such as acid concentration and temperature [14]. The corrosion rate of carbon steel is high for concentrations of H_2SO_4 lower than 50%.

The predicted furnace temperature is compared with field data for the 30% and 50% H_2S acid gas cases in Fig. 5. These results indicate that oxygen enrichment will have a significant direct effect on the furnace temperature and for many acid gas feeds, will bring the furnace temperature to above the 1050 °C threshold. These results indicate that the furnace temperature will increase between 25 and 50 °C for each 10% increase in equivalent oxygen content. The simulated results are in good agreement with the field data as shown in Fig. 5.

8. Acid gas enrichment

With the advent of selective amine systems, it is possible to improve the quality of an acid gas stream in an amine treating unit [1]. Some of the existing plants utilize this

technology to improve the acid gas for variety of reasons. Acid gas enrichment has two important benefits:

1. Providing a high quality acid gas for processing in a Claus SRU.
2. Decreasing the acid gas flow rate and the size of SRU.

The acid gas enrichment should be used with care, considering the Claus process characteristics. If a lack of air occurs, less than 1/3 of H_2S will react and the H_2S will then be in excess. There are different forms of carbon and stainless steel corrosion when in contact with a H_2S environment namely; sulfide stress cracking, hydrogen stress cracking, hydrogen blistering, localized corrosion (pitting) [16–18], and cracking in the welded region [19]. The H_2S accelerates the hydrogen absorption in steel [20]. The hydrogen sulfide reacts with iron in the presence of water and the produced hydrogen migrates to the high stress concentration regions in the metal. The presence of hydrogen in steel facilitates the motion of the linear effects in the crystalline structure of metal. Vagapov et al. [20] concluded that the steel hydrogenation in a vapor phase occurs with the same intensity as in the aqueous phase.

The effect of increasing the H_2S content of the acid gas on the furnace temperature is predicted by the proposed model and illustrated in Fig. 6. It is clear that increasing the H_2S content of the acid gas will significantly increase the furnace temperature. It is interesting to take a problem acid gas stream containing levels of H_2S that are too low ($H_2S < 20\%$) for use in a Claus SRU (and probably too high for flaring) and produce a very high quality Claus SRU acid gas feed. According to Fig. 6, the H_2S content is increased to in excess of 60 mol% to ensure a furnace temperature above the desired minimum value of 1050 °C. The experimental data are gathered from a MDEA based acid gas enrichment unit followed by a Claus reaction furnace. The predicted results are in close agreement with the measured values as shown in Fig. 6.
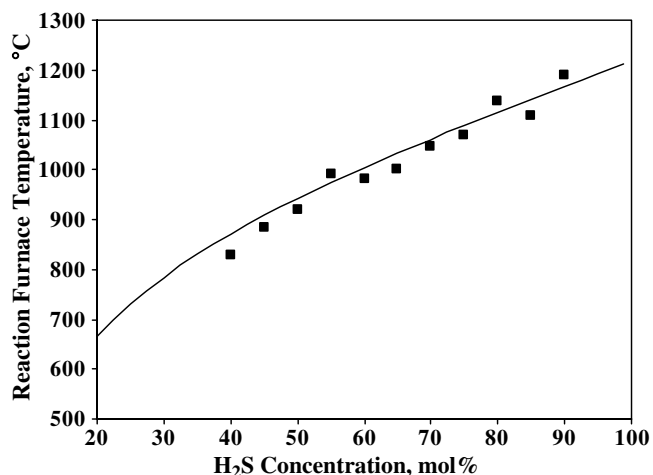

Fig. 6. Effect of acid gas enrichment on reaction furnace temperature (-model prediction, experimental data: ■ 40% H_2S).

9. Conclusions

Many Claus sulfur recovery units suffer from poor flame stability and hydrocarbon destruction in the reaction furnace due to a low reaction furnace flame temperature. This is normally a symptom of poor acid gas feed quality. In order to mitigate this problem, several commercially viable techniques available for increasing the furnace temperature such as fuel gas spiking, air and acid gas preheating, direct fuel gas air preheating, oxygen enrichment and acid gas enrichment are evaluated by chemical equilibrium calculations. The Gibbs free minimization method is used for simultaneous prediction of reaction furnace temperature and optimum air flow rate of Claus sulfur recovery units at different operating conditions and the predicted results are compared with experimental data. While each of these methods will result in a measurable improvement in the furnace temperature, any one method by itself may not be adequate to meet the desired minimum furnace temperature. In the case of lean feed acid gases, it may be necessary to use a combination of techniques in order to attain the minimum furnace temperature required for flame stability and complete destruction of problem hydrocarbon contaminants. The acid gas enrichment is an interesting alternative for handling very lean acid gases, especially when the rate of acid gas is too high. Considering the assumptions made for model development, the predicted results are in good agreement with the field data.

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