The thermodynamics and kinetics of the Molten-Iron-Pure-Gas (MIP) process used for coal gasification have been analyzed. In the MIP process, oxygen, fine-grained coal, and fluxes are injected into a liquid iron bath to produce a high temperature gas consisting of CO and H₂ plus a liquid basic slag. The sulfur is transferred from the coal to this slag. Computer calculations bearing in mind test conditions were used to determine equilibrium conditions as well as mass and energy balances; these indicated that the MIP process is technically feasible. The kinetics of the gasification process have been investigated by analyzing and assessing the basic reactions for a bottom-blowing MIP reactor. A comparison of all relevant reactions reveals that the dissolution of carbon in iron is the rate-determining step of the process. The bath turbulence induced by the injected gas and by the product gas results in intense mixing and dispersion of the reactants and their intermediate products. These phenomena create extremely large mass-transfer surfaces and extend the retention time of the reactants in the liquid iron bath. This results in high conversion rates relative to the volume of the MIP reactor.

II. THERMODYNAMICS

A. Basis of Calculations

For thermodynamic calculations, coal gasification in a liquid iron bath is considered as a steady-state flow process in an isothermal-isobaric reactor. As shown schematically in Figure 1, coal, oxygen, and other feed materials are considered as reacting with each other in the reactor until equilibrium or a defined approach to equilibrium has been reached. The product gas containing dust is assumed to leave the reactor continuously, with the liquid slag being withdrawn either continuously or batchwise.

The equilibrium phases and main components contained in the reactor may be represented by:

- Liquid iron bath: Fe, C, S, Si;
- Slag: CaO, CaS, SiO₂, Al₂O₃, K₂O, MgO;
- Gas phase: CO, H₂, CO₂, H₂S, CH₄.

In this paper the liquid iron bath has, for reasons of simplicity, been assumed to be an Fe-C-S alloy. Slag constituents have been considered to be simple compounds instead of ions. The gas phase has been assumed to be ideal.

Fig. 1 — Schematic representation of coal gasification in the liquid iron bath as a stationary flow process.

[Diagram of coal gasification process]

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Apart from the three equilibrium phases mentioned, mass and energy balances must account for the dust entrained in the product gas. The composition and quantity of the dust have been based on test results. Similar considerations apply to the dissolution of the reactor brick lining during gasification. The overall process is autothermal. The heat transfer from the reactor to its environment is balanced by the net reaction enthalpy so that a constant temperature profile is assumed.

Thermodynamic calculations were performed with the aid of computer programs and data base including Eriksson's SOLGASMIX program. Quantities and ratios of feed materials necessary for the desired product compositions were ascertained by iterative variations.

B. Thermochemical Data

The thermochemical data for pure substances were acquired from data compilations. The activity coefficients of the components of the Fe-C-S system have been calculated using equations from the quadratic formalism introduced by Darken. The activity of the component is defined as:

\[ a_i = X_i \gamma_i \]  

where \( X_i \) denotes the atom (mole) fraction and \( \gamma_i \) the activity coefficient. From equations and parameters given in Reference 14 the following relations have been derived for the concentration range:

\[ \log \gamma_F = -2.51X_F - 3.66X_S \]  

\[ \log \gamma_C = -2.51[(1 - X_F)^3 - (1 - X_C^m)^3] - \log X_C^m \]  

\[ \log \gamma_S = -2.51X_C^2 + 3.66X_C - 1.67X_S \]  

The standard states are pure liquid iron for Fe, graphite for C, and infinite dilute solution for S. \( \gamma_S \) stands for the ratio of the activity coefficient \( \gamma_S \) of S in the Fe-C-S system and the Henrian coefficient \( \gamma_S \) in the Fe-S system, i.e., \( \gamma_S = \gamma_S(Fe-C-S)/\gamma_S(Fe-S) \). The numerical coefficients in Eqs. [2], [3], and [4] have been calculated by temperature shift of values specified in Reference 14 with the assumption that the coefficients were inversely proportional to \( T \).\( X_C^m \) in Eq. [3] denotes the mole fraction of C at graphite saturation of liquid Fe and is represented by the following relation:

\[ \log X_C^m = -560/T - 0.375 \]  

Equations [2] and [3] apply for a relatively wide concentration range leading to activity values which are in satisfactory accord with experimental data. Sulfur activities calculated using Eq. [4] in combination with solution data from the binary Fe-S system are in agreement with the experimental data from the ternary Fe-C-S system.

Accurate data for the activity coefficients of the slag components are not available. To determine the equilibrium concentration of S in the liquid slag, the following relations were used:

\[ O^{2-}(\text{slag}) + \frac{1}{2}S_2(\text{gas}) = S^{2-}(\text{slag}) + \frac{1}{2}O_2(\text{gas}) \]  

\[ C_5 = (\text{wt pct } S)_{\text{log}} \left(\frac{P_{O_2}/P_{S_2}}{2}\right)^{1/2} \]  

In Eq. [6b] \( C_5 \) is the sulfur capacity for which the following relation was derived from the data reported by Venkatradi and Bell at \( T = 1773 \) K:

\[ \log C_5 = 1.38\frac{X_{CaO} + X_{MgO}/2}{X_{SiO_2} + X_{Al_2O_3}/3} - 5.59 \]  

After calculation of gas-iron bath equilibrium, \( X_{CaO} \) was determined via the amount of CaO (lime input) by iterative variations using Eqs. [6] and [7] until sulfur equilibrium was reached, with allowance being made for the mass balance.

C. Calculation Parameters and Results

The following conditions were assumed for the calculations: \( T = 1773 \) K, \( P = 10^5 \) Pa, wt pct C (dissolved in Fe) = 3.5, total S content of product gas = 100 vol ppm. Further data, such as the composition of coal and other feed materials, the quantity and composition of the entrained dust, and the reactor heat losses, were taken from preliminary tests with a converter containing 3000 kg Fe. The specific reactor throughput was assumed to be 500 kg coal per hour and 1000 kg liquid iron bath.

Table I presents the overall mass and enthalpy balance related to a throughput of 1000 kg of coal. For the case under discussion, the net enthalpy for the reactions was calculated to be \(-0.160 \) GJ corresponding to the heat losses of the reactor to the environment. For a given product quality, the energy balance is strongly influenced by the composition of the feed materials, in particular by the composition of the coal. In special cases, depending on the calorific value of the coal feed, preheated air or preheated oxygen-air mixtures instead of pure oxygen may be used as gasification agent.

The compositions of the coal feed and entrained dust are given in Table IIa. Table IIb shows the compositions of the produced slag and gas phase for the equilibrium state at \( 10^5 \) Pa and 1773 K. The gas phase consists mainly of CO.