The Effect of Noncondensables on the
Work Output of Geothermal-Steam Systems

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NOTICE

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Scope

In this note we study the influence of noncondensables on the output work from geothermal steam power plants. Two problems are addressed: the effect of CO_2 on the exergy (available work) of a given mixture of steam and CO_2 and secondly, the effect of CO_2 on the expansion work of an ideal turbine exhausting at a given back pressure. The results in the latter case are also modified to account for the influence of CO_2 on the dryness of the exhaust mixture and the corresponding effect on the expansion efficiency.

Introductory remarks

When a geothermal water that contains dissolved CO_2 is flashed to a low pressure, practically all the dissolved CO_2 is liberated in the flash tank where, ideally, it exists in equilibrium with the H_2O component. The latter exists both as a liquid and as a vapor. Owing to the low solubility of CO_2 in water, especially at low pressures and temperatures, the liquid phase can be regarded as pure water in equilibrium with the steam component of the gaseous phase. That is to say that the chemical potentials of H_2O in the liquid and vapor phases are equal and so are the chemical potentials of CO_2

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in the two phases. However, the CO_2 insolubility assumption implies that the chemical potential of CO_2 in the CO_2 - H_2O system is infinite. Bearing this in mind we consider a gaseous mixture of steam and CO_2 at a temperature T_1 in which the steam exists at the saturation state corresponding to T_1 .

The mass fraction of CO_2 present in this mixture is designated by f . The thermodynamic state of CO_2 in the mixture can be determined if we assume that the gases behave as ideal gases. In this case the total pressure of the mixture, P_1 , is given by

$$P^{(1)} = P_{\text{CO}_2}^{(1)} + P_{\text{H}_2\text{O}}^{(1)}, \quad (1)$$

where $P_{\text{H}_2\text{O}}^{(1)} = P_v(T_1)$. The partial pressure of CO_2 is related to the partial pressure of H_2O through the mole fraction, v , which depends in turn on the mass fraction, i.e.

$$v_1 = \left[\frac{f/M_{\text{CO}_2}}{\left\{ \left[\frac{f}{M_{\text{CO}_2}} \right] + \left[\frac{(1-f)}{M_{\text{H}_2\text{O}}} \right] \right\}} \right]. \quad (2)$$

$$= \mu f / [\mu f + 1 - f]. \quad (2')$$

Here M refers to the molecular mass and μ is the ratio $M_{\text{H}_2\text{O}}/M_{\text{CO}_2} = 0.4092$.

Now we can write

$$P_{\text{CO}_2}^{(1)} = v_1 P_v(T_1) / (1 - v_1). \quad (3)$$

The enthalpy and entropy of the inlet mixture can then be obtained:

$$h_{\text{mix}}^{(1)} = f h_{\text{CO}_2}(T_1) + (1-f) h_{\text{H}_2\text{O}}''(T_1), \quad (4)$$

$$s_{\text{mix}}^{(1)} = f s_{\text{CO}_2}(T_1, P_{\text{CO}_2}^{(1)}) + (1-f) s_{\text{H}_2\text{O}}''(T_1). \quad (5)$$

In these equations the enthalpy of CO_2 depends only on temperature as implied by the ideal-gas assumption. The enthalpy and entropy of H_2O depends only on temperature as implied by the conditions for phase equilibrium; these are the saturated vapor properties at T_1 . The entropy of CO_2 is calculable from the ideal gas fundamental equation as

$$s_{\text{CO}_2}^{(1)} = s^* (P^*, T^*) + \int_{T^*}^{T_1} c_p dT/T - R \ln P_{\text{CO}_2}^{(1)}/P^* , \quad (6)$$

in which the stars refer to a reference state. Since changes in entropy and not entropy itself is what interests us here, we can choose $s^* = 0$. Furthermore, for a thermally-perfect gas, c_p is independent of temperature, thus

$$s_{\text{CO}_2}^{(1)} = c_p \ln T_1/T^* - R \ln P_{\text{CO}_2}^{(1)}/P^* . \quad (7)$$

Exergy

The calculation of the exergy (available work) associated with this mixture requires the definition of a dead state. A natural choice for the problem at hand is an equilibrium mixture of CO_2 - H_2O at the ambient pressure, P_o and the ambient temperature T_o . This mixture will consist of a liquid phase made essentially of pure H_2O and a gaseous mixture of CO_2 and H_2O in equilibrium with the liquid. Thus

$$P_{\text{H}_2\text{O}}^o = P_v (T_o) , \quad (8)$$

and

$$v_o = 1 - P_v (T_o)/P_o . \quad (9)$$

The mass fraction, f_o , of CO_2 in the gaseous mixture is related to v_o by

$$f_o = v_o / [v_o + (1-v_o) \mu] \quad . \quad (10)$$

Conservation of mass necessitates that the dryness fraction, x , of the H_2O component be related to f and f_o by

$$x = f(1-f_o)/f_o(1-f) \quad . \quad (11)$$

The enthalpy and entropy of the system at the dead state can thus be determined

$$h^{(o)} = f h_{CO_2}(T_o) + x(1-f) h''_{H_2O}(T_o) + (1-x)(1-f) h'_{H_2O}(T_o) \quad , \quad (12)$$

$$s^{(o)} = f s_{CO_2}(T_o, P_{CO_2}^{(o)}) + x(1-f) s''_{H_2O}(T_o) + (1-x)(1-f) s'_{H_2O}(T_o) \quad . \quad (13)$$

The expression for exergy (available work) is

$$W^o = h^{(1)} - h^{(o)} - T_o (s^{(1)} - s^{(o)}) \quad . \quad (14)$$

Upon substituting for the various quantities we obtain

$$\begin{aligned} W^o = & f c_p (T_1 - T_o) + (1-f) \left[h''_{H_2O}(T_1) - h'_{H_2O}(T_o) - x L_o \right] - \\ & T_o \left\{ f \left[c_p \ln (T_1/T_o) - R \ln \left(P_{CO_2}^{(1)}/P_{CO_2}^{(o)} \right) \right] + \right. \\ & \left. (1-f) \left[s''_{H_2O}(T_1) - s'_{H_2O}(T_o) - x L_o/T_o \right] \right\} \quad , \quad (15) \end{aligned}$$

in which L_o is the latent heat of H_2O at T_o .

Figure 1 shows the normalized available work for the H_2O - CO_2 system for $T_1 = 125, 150, 175, 200^\circ C$. The work is normalized with respect to the value

corresponding to uncontaminated steam. The dead state temperature is 298.15 K and the dead state pressure is 0.1 MPa (~ 1 atm). It can be seen that the dependence of the normalized work on initial temperature is weak and that the effect of CO_2 is such that the normalized available work drops by about 1% for each 1% mass increment of CO_2 .

Turbine expansion work

In this section we consider the adiabatic expansion of a mixture of saturated steam and CO_2 at temperature T_1 down to a given back pressure P_2 . In the ideal case the mixture will follow an isentropic expansion line. The enthalpy and entropy of the mixture at state (1) are given by eqs. (4) and (5) respectively. At state (2) a mixture of CO_2 , H_2O vapor and H_2O liquid will exist at a temperature T_2 lower than the steam saturation temperature corresponding to P_2 . The determination of this temperature requires iteration as we will show below. Assuming that the value of T_2 has been found, the determination of the properties at state (2) proceeds as we described for state (0) in the previous section. Naturally the correct value of T_2 is that which satisfies the constraint

$$s_{\text{mix}}^{(2)} = s_{\text{mix}}^{(1)} \quad (16)$$

In an iterative procedure, a trial value of T_2 is selected and the entropy at state (2) corresponding to this trial value is calculated and compared with the initial value of the entropy. The value of T_2 is then incremented until condition (16) is satisfied within an acceptable tolerance.

The nature of the equation employed for these calculations indicates that obtaining the steam properties by interpolating in the steam tables results in large numerical uncertainties. This is particularly true as the mass fraction of CO_2 tends to zero since one of the equations [eq. (11)] becomes

indeterminate. For this reason we employed the Clausius-Clapeyron equation for the determination of the saturated steam properties at exhaust conditions.

The Clausius-Clapeyron equation was integrated after substituting a linear expression for the latent heat and a perfect gas law for the saturated vapor, i.e.

$$L/(kJ/kg) = 3156.2 - 2.394 (T/K) \quad (17)$$

$$v'' = RT/P_v \gg v' \quad (18)$$

This leads to the following expression for the vapor pressure in the temperature range $298.15 < T < 333.15$ K:

$$\ln [P_v/0.003169 \text{ MPa}] = (1-298.15 \text{ K}/T) - 5.183 \ln (T/298.15 \text{ K}). \quad (19)$$

Furthermore, the enthalpy and entropy of the saturated liquid were evaluated on the assumption that the liquid behaves as an incompressible fluid with a constant specific heat. Thus

$$h'/(kJ/kg) = 4.187 (T-273.15)/K, \quad (20)$$

and

$$s'/(kJ/kg \text{ K}) = 4.187 \ln (T/273.15 \text{ K}),$$

in which we assumed that the data of enthalpy and entropy are located at $T = 273.15$ K.

The normalized expansion work for various initial temperatures and a fixed back pressure of 0.012349 MPa is shown as a function of f in Fig. 2. It is seen that the dependence on T_1 is weak and that approximately a loss

of 0.5% occurs for each increment of 1% in the mass fraction of CO_2 . It was also noticed that the presence of CO_2 results in a depression of the exhaust temperature amounting to as much as 4°C beyond the saturation value corresponding to P_2 (50°C).

The presence of CO_2 in the exhaust mixture alters its dryness fraction defined here by

$$x(f) = f + x(1-f) . \quad (22)$$

Since the expansion efficiency in a nonideal situation depends, among other factors, on the percentage moisture present as indicated by Baumann's rule, it is expected that the actual value of normalized work $W_a(f)/W_a(o)$ will exhibit dependence on the dryness fractions. Therefore we write

$$W_a(f)/W_a(o) = \xi W^o(f)/W^o(o) , \quad (23)$$

in which ξ is the ratio of the isentropic expansion efficiencies with and without CO_2 , i.e.

$$\xi = \eta(f)/\eta(o) . \quad (24)$$

If we adopt the Baumann rule for the evaluation of the wetness effect on the expansion efficiency we obtain

$$\xi = x(f)/x(o) . \quad (25)$$

Figure 3 demonstrates the dependence of ξ on the mass fraction of CO_2 for various initial temperatures. The effect of this modifier on the normalized work is represented by the dashed lines in Fig. 2. It can be seen that the

effect of CO_2 is such that the effective dryness fraction of the exhaust mixture is somewhat higher. This results in attenuating the rate at which the expansion work declines with increasing CO_2 mass fraction.

Figure 1

Figure 2

Figure 3