Lecture 13: Calcination

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Key words: calcination, electrolysis of alumina, fuel saving

Principles of calcination:

Calcination is a thermal treatment process and applied to ores and other solid materials to bring

a) thermal decomposition
b) phase transition and
c) to remove volatile fractions such as CO₂, H₂O

Material is heated below the melting point in rotary kiln or fluidized bed reactor. Calcination is done in the solid state.

Application:

✔ To produce cement from CaCO₃
✔ To cause decomposition of hydrated minerals as in calcination of bauxite to produce refractory grade Al₂O₃.
✔ To cause decomposition of volatile matter contained in petroleum Coke.
✔ To heat treat to effect phase transformation as in devitrification of glass materials.
✔ To produce anhydrousAl₂O₃ for electrolysis of Al₂O₃ to Al in Hall-Heroult cell

Materials and heat balance in calcination
Calcination requires thermal energy. This is illustrated by solving few problems. For calculation, we need several thermo chemical values like heat of formation, specific heat, and heat content. The following thermo chemical values are used to solve the problems in this lecture:

Thermo chemical values:

\[
\begin{align*}
\text{CaCO}_3 & = \text{CaO} + \text{CO}_2 & \Delta H_f^0 & = +42750 \text{ Kcal/Kg.mol} \\
\text{MgCO}_3 & = \text{MgO} + \text{CO}_2 & \Delta H_f^0 & = +24250 \text{ Kcal/Kg.mol} \\
\text{CO} + \frac{1}{2} \text{O}_2 & = \text{CO}_2 & \Delta H_f^0 & = -67900 \text{ Kcal/Kg.mol} \\
2\text{Al(OH)}_3 & = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} & \Delta H_f^0 & = +24290 \text{ Kcal/Kg.mol} \\
\text{C} + \text{O}_2 & = \text{CO}_2 & \Delta H_f^0 & = -94300 \text{ Kcal/Kg.mol} \\
\text{H}_2 + \frac{1}{2} \text{O}_2 & = \text{H}_2\text{O} & \Delta H_f^0 & = -68370 \text{ Kcal/Kg.mol} \\
\end{align*}
\]

\[
\begin{align*}
\text{Cp}_{\text{CaO}} & = 49.622 + 4.519 \times 10^{-3} T - 6.945 \times 10^5 T^{-2} \text{ kJ/Kg.mol K} \\
\text{Cp}_{\text{MgO}} & = 48.995 + 3.138 \times 10^{-3} T - 11.715 \times 10^5 T^{-2} \text{ kJ/Kg.mol K} \\
\text{Cp}_{\text{CO}_2} & = 75.438 \text{ kJ/Kg.mol K} \\
\text{Cp}_{\text{H}_2\text{O(v)}} & = 30. + 10.711 \times 10^{-3} T - 0.335 \times 10^5 T^{-2} \text{ kJ/Kg.mol K} \\
\end{align*}
\]

Heat content

\[
\begin{align*}
\text{H}_{1200} - \text{H}_{298} | \text{CaO} & = 10800 \text{ Kcal/Kg.mol} \\
\text{H}_{500} - \text{H}_{298} | \text{CO}_2 & = 1987 \text{ Kcal/Kg.mol} \\
\text{H}_{500} - \text{H}_{298} | \text{N}_2 & = 1418 \text{ Kcal/Kg.mol} \\
\text{H}_{500} - \text{H}_{298} | \text{O}_2 & = 1455 \text{ Kcal/Kg.mol} \\
\text{H}_{1000} - \text{H}_{298} | \text{Al}_2\text{O}_3 & = 18710 \text{ Kcal/Kg.mol} \\
\text{H}_{800} - \text{H}_{298} | \text{CO}_2 & = 5458 \text{ Kcal/Kg.mol} \\
\text{H}_{800} - \text{H}_{298} | \text{O}_2 & = 3786 \text{ Kcal/Kg.mol} \\
\text{H}_{800} - \text{H}_{298} | \text{N}_2 & = 3598 \text{ Kcal/Kg.mol} \\
\text{H}_{800} - \text{H}_{298} | \text{H}_2\text{O(l)} & = 14824 \text{ Kcal/Kg.mol} \\
\text{H}_{900} - \text{H}_{298} | \text{CO}_2 & = 6708 \text{ Kcal/Kg.mol} \\
\text{H}_{900} - \text{H}_{298} | \text{O}_2 & = 4602 \text{ Kcal/Kg.mol} \\
\text{H}_{900} - \text{H}_{298} | \text{N}_2 & = 4358 \text{ Kcal/Kg.mol} \\
\text{H}_{900} - \text{H}_{298} | \text{CO} & = 4400 \text{ Kcal/Kg.mol} \\
\end{align*}
\]

Latent Heat of vaporization of water = 10520 kJ/kg.mol

**Problem-i: decomposition of CaCO\textsubscript{3}**
1) Calculate the heat energy required to calcine 1000 Kg limestone of composition 84% CaCO₃, 8% MgCO₃ and 8% H₂O charged at 298K. Lime is discharged at 1173K and gases leave at 473K.

Solution:

\[
\begin{align*}
\text{CaCO}_3 &= \text{CaO} + \text{CO}_2 \\
\text{MgCO}_3 &= \text{MgO} + \text{CO}_2
\end{align*}
\]

(1) (2)

Material balance gives

Calcined product and gases

\[
\begin{align*}
\text{CaO} &= 8.4 \text{ kg mols} \\
\text{MgO} &= 0.952 \text{ kg mols} \\
\text{CO}_2 &= 9.352 \text{ kg mols} \\
\text{H}_2\text{O} &= 4.444 \text{ kg mols}
\end{align*}
\]

Heat of decomposition of reaction 1 and 2 = 382186 k cal.

Using Cp values one can calculate sensible heat in calcined products and gases. Reference state is 298K.

Sensible heat in products = \(8.4 \int_{298}^{1173} \text{Cp (CaO)} \, dT + 0.952 \int_{298}^{1173} \text{Cp (MgO)} \, dT\)

Sensible heat in \(\text{CO}_2\) = \(9.352 \int_{298}^{473} \text{Cp (CO}_2\) \, dT\)

Sensible heat in \((\text{H}_2\text{O})\text{l})\) can be evaluated as

\[
\begin{align*}
(\text{H}_2\text{O})_{l,298} &= (\text{H}_2\text{O})_{l,373} \\
(\text{H}_2\text{O})_{l,373} &= (\text{H}_2\text{O})_{v,373} \\
(\text{H}_2\text{O})_{v} &= 4.44 \int_{298}^{473} \text{Cp(H}_2\text{O)} \, dT
\end{align*}
\]

Heat energy required = \(2.17 \times 10^6 \text{ kJ}\) Answer

Problem 2: amount of fuel in calcination

It is desired to produce 10 kg. mol lime from calcinations of CaCO₃ (pure) in a rotary kiln. Producer gas of composition CO₂ 7.2%, O₂ 1.6%, CO 16.6% and N₂ 74.6% is combusted with 20% excess air to obtain the desired temperature in the kiln. The limestone and air are supplied at 298K, whereas producer gas is heated to 900K. Lime is discharged at 1200 K and at 500K.
Calculate the amount of producer gas (1 atm. and 273 K).

Let Y kg mol is the producer gas

Material balance gives

\[
\begin{align*}
\text{CO}_2 &= 10 + 0.238 Y \\
\text{N}_2 &= 0.74 Y + 0.302 Y \\
\text{O}_2 &= 0.0134 Y
\end{align*}
\]

Calorific value of producer gas= 11271 Y kcal.


Sensible heat in producer gas+ calorific value of producer gas – Heat of decomposition of CaCO\(_3\) = sensible heat in CaO + sensible heat in flue gases (\text{CO}_2, \text{N}_2 \text{ and } \text{O}_2)

We calculate all the values and get \( Y = 40.15 \text{ kg moles and is equal to 899 m}^3 \) Answer

**Problem 3 Calcination of Al(OH)\(_3\)**

In the electrolysis, anhydrous alumina is required. For this purpose Al(OH)\(_3\) is calcined at 1700 K in rotary kiln. A kiln receives a damp filter cake of Al(OH)\(_3\) analyzing 55\% Al\(_2\)O\(_3\) and 45\% total H\(_2\)O (free and combined) and produce, pure Al\(_2\)O\(_3\) as solid product. The fuel consumption is estimated to be 0.2Kg of fuel oil of composition 84\% C and 16\% H per Kg of alumina. Air for combustion is 20\% excess than theoretical required. Assume complete combustion and heat losses 10\% of heat input. Find

a) The volume of gases (At 1 atm, 273 K) leaving the kiln per 1000Kg of Al\(_2\)O\(_3\) produced.
b) Wet and dry composition of flue gases.
c) Perform the heat balance and comment on the results. Assume reactants enter at 298K and products namely Al\(_2\)O\(_3\) at 1000K and flue gases at 800K.

Solution: Basis of calculation 1000Kg calcineAl\(_2\)O\(_3\)

Calcination reaction:

\[2\text{Al(OH)}_3 = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}\]

Combustion reactions

\[\text{C} + \text{O}_2 = \text{CO}_2\]

\[2\text{H} + 0.5\text{O}_2 = \text{H}_2\text{O}\]

Material balance gives volume of flue gases 4014 m\(^3\)
Flue gas analysis: on Wet basis (%) | On dry basis (%)
---|---
CO₂ 7.8 | 11.9
O₂ 2.5 | 3.7
N₂ 55.4 | 84.4
H₂O 34.3 | -
100% | 100%

Heat balance gives the following result:

<table>
<thead>
<tr>
<th>Heat input (kcal)</th>
<th>Heat output (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion of fuel +2414120*</td>
<td>Flue gases 1362135</td>
</tr>
<tr>
<td>Heat of decomposition – 238137⁰</td>
<td>Sensible heat in Al₂O₃ 183431</td>
</tr>
<tr>
<td>Heat available: 2175983</td>
<td>Heat losses 217598</td>
</tr>
<tr>
<td></td>
<td>Total 1763164 kcal</td>
</tr>
</tbody>
</table>

* + indicated heat input due to exothermic and - indicates heat absorption.

**Heat balance indicates that there is 412819 kcal heat is surplus. This surplus heat may be utilized. If not then amount of fuel may be reduced as illustrated in problem 4**

**Problem 4: Fuel saving**

Calculate the minimum amount of fuel 1000Kg Al₂O₃. Use the data given in problem 3.

Let x kg fuel is required.

C = 0.84 x and H = 0.16 x

We have to calculate flue gas. The calculation gives kg mols

\[
CO₂ = 0.07 x \\
H₂O = 0.08x + 45.45 \\
O₂ = 0.022 x \\
N₂ = 0.496 x
\]

**Heat balance:**

Heat of combustion = Heat taken by flue gas + Heat taken by Al₂O₃ + heat losses
Performing heat balance calculation, we can get

\[ x = 141 \text{kg fuel} \] is required to produce 1000Kg alumina.

We save \( 200 - 141 = 59 \text{ fuel kg fuel oil /1000 Kg Al}_2\text{O}_3 \)

Conclusion:

This lecture discusses the basics of calcination by solving problems. The importance of heat balance calculations is shown in problem 4 which shows that fuel saving can be achieved.

References:

