

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 CO_2 , H_2O

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 CaCO_3
- ✓ To cause decomposition of hydrated minerals as in calcination of bauxite to produce refractory grade Al_2O_3 .
- ✓ 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 anhydrous Al_2O_3 for electrolysis of Al_2O_3 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:

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

$$C_{p_{\text{CaO}}} = 49.622 + 4.519 \times 10^{-3} T - 6.945 \times 10^{-5} T^{-2} \text{ kJ/Kg.mol K}$$

$$C_{p_{\text{MgO}}} = 48.995 + 3.138 \times 10^{-3} T - 11.715 \times 10^{-5} T^{-2} \text{ kJ/Kg.mol K}$$

$$C_{p_{\text{CO}_2}} = 75.438 \text{ kJ/Kg.mol K}$$

$$C_{p_{\text{H}_2\text{O}(v)}} = 30. + 10.711 \times 10^{-3} T - 0.335 \times 10^{-5} T^{-2} \text{ kJ/Kg.mol K}$$

Heat content

$H_{1200} - H_{298} \text{CaO}$	=10800	Kcal/Kg.mol
$H_{500} - H_{298} \text{CO}_2$	=1987	Kcal/Kg.mol
$H_{500} - H_{298} \text{N}_2$	=1418	Kcal/Kg.mol
$H_{500} - H_{298} \text{O}_2$	=1455	Kcal/Kg.mol
$H_{1000} - H_{298} \text{Al}_2\text{O}_3$	=18710	Kcal/Kg.mol
$H_{800} - H_{298} \text{CO}_2$	=5458	Kcal/Kg.mol
$H_{800} - H_{298} \text{O}_2$	=3786	Kcal/Kg.mol
$H_{800} - H_{298} \text{N}_2$	= 3598	Kcal/Kg.mol
$H_{800} - H_{298} \text{H}_2\text{O}(l)$	= 14824	Kcal/Kg.mol
$H_{900} - H_{298} \text{CO}_2$	= 6708	Kcal/Kg.mol
$H_{900} - H_{298} \text{O}_2$	= 4602	Kcal/Kg.mol
$H_{900} - H_{298} \text{N}_2$	= 4358	Kcal/Kg.mol
$H_{900} - H_{298} \text{CO}$	= 4400	Kcal/Kg.mol

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

Problem-i: decomposition of CaCO_3

- 1) Calculate the heat energy required to calcine 1000Kg limestone of composition 84%CaCO₃, 8%MgCO₃ and 8% H₂O charged at 298K. Lime is discharged at 1173K and gases leave at 473K.

Solution:



Material balance gives

Calcined product and gases

$$\text{CaO} = 8.4 \text{ kg mols}$$

$$\text{MgO} = 0.952 \text{ kg mols}$$

$$\text{CO}_2 = 9.352 \text{ kg mols}$$

$$\text{H}_2\text{O} = 4.444 \text{ kg mols}$$

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

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

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

Sensible heat in H₂O(l) can be evaluated as

$$(\text{H}_2\text{O})_{l,298} = (\text{H}_2\text{O})_{l,373}$$

$$(\text{H}_2\text{O})_{l,373} = (\text{H}_2\text{O})_{v,373}$$

$$(\text{H}_2\text{O})_v = 4.44 \int_{298}^{473} C_p(\text{H}_2\text{O})_v dT$$

Heat energy required = 2.17 × 10⁶ 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

$$\text{CO}_2 = 10 + 0.238 Y$$

$$\text{N}_2 = 0.74 Y + 0.302 Y$$

$$\text{O}_2 = 0.0134 Y$$

Calorific value of producer gas= 11271 Y kcal.

Performing heat balance: Heat input= Heat output.

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 (CO_2 , N_2 and O_2)

We calculate all the values and get Y = 40.15 kg moles and is equal to 899 m³ Answer

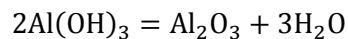
Problem 3 Calcination of $\text{Al}(\text{OH})_3$

In the electrolysis, anhydrous alumina is required. For this purpose $\text{Al}(\text{OH})_3$ is calcined at 1700 K in rotary kiln. A kiln receives a damp filter cake of $\text{Al}(\text{OH})_3$ analyzing 55% Al_2O_3 and 45% total H_2O (free and combined) and produce, pure Al_2O_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

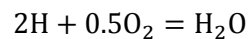
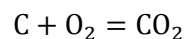
- The volume of gases (At 1 atm, 273 K) leaving the kiln per 1000Kg of Al_2O_3 produced.
- Wet and dry composition of flue gases.
- Perform the heat balance and comment on the results. Assume reactants enter at 298K and products namely Al_2O_3 at 1000K and flue gases at 800K.

Solution: Basis of calculation 1000Kg calcine Al_2O_3

Calcination reaction:



Combustion reactions



Material balance gives volume of flue gases 4014 m³

Flue gas analysis: on Wet basis (%)	On dry basis (%)
CO ₂ 7.8	11.9
O ₂ 2.5	3.7
N ₂ 55.4	84.4
H ₂ O 34.3	-
100%	100%

Heat balance gives the following result:

Heat input (kcal)	Heat output (kcal)
Combustion of fuel +2414120*	Flue gases 1362135
Heat of decomposition – 238137 ⁰	Sensible heat in Al ₂ O ₃ 183431
	Heat losses 217598
Heat available: 2175983	Total 1763164 kcal

* + 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 problem3.

Let x kg fuel is required.

$$C = 0.84x \text{ and } H = 0.16x$$

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

$$CO_2 = 0.07x$$

$$H_2O = 0.08x + 45.45$$

$$O_2 = 0.022x$$

$$N_2 = 0.496x$$

Heat balance:

$$\text{Heat of combustion} = \text{Heat taken by flue gas} + \text{Heat taken by Al}_2\text{O}_3 + \text{heat losses}$$

Performing heat balance calculation, we can get

$x = 141$ kg fuel is required to produce 1000 Kg alumina.

We save $200 - 141 = 59$ fuel kg fuel oil /1000 Kg Al_2O_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.

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- 2) Butts, Allison: Metallurgical Problems, McGraw Hill Book Company, 1943
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