

Lecture 14: Pyro metallurgical extraction (Roasting)

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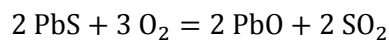
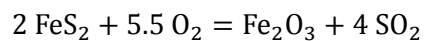
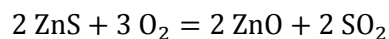
Keywords: roasting, dead roasting, sulphatizing roasting

Introduction:

In Pyro metallurgical extraction of metal, thermal energy is one of the important inputs. Different unit processes like roasting, smelting, converting and refining require large amount of thermal energy. This lecture discusses roasting.

Roasting

Roasting is the oxidation of metal sulphides to give metal oxides and sulphur dioxide. Typical examples are:



In addition other reactions may take place: formation of SO_3 and metal sulphates and formation of complex oxides such as $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$.

Typically, sulphide ores of copper, zinc and lead are roasted either partially or completely. Copper sulphide ores are roasted partially; whereas ores of lead and Zinc are roasted completely into oxides for subsequent treatment. This SO_2 is then a byproduct.

Roasting is usually carried out below the melting points of the sulphides and oxides involved, usually below $900 - 1000^\circ\text{C}$. Both reactants and products are in the solid state.

In roasting ore concentrate is mixed with for oxidation. Normally excess air is used for roasting. Fuel may or may not be used.

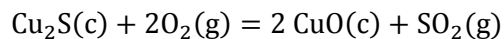
Sources of energy

Different sources of thermal energy are

- a) Heat of reaction: Combustion of S to SO_2 or SO_3 releases -70940 k cal/kg mol and -93900 k cal/kg mol of thermal energy respectively. Several oxidation reactions like $\text{Fe} - \text{Fe}_2\text{O}_3$, $\text{FeS} \rightarrow \text{FeO}$, $\text{ZnS} - \text{ZnO}$ and so on releases thermal energy. These energies can be calculated from the heat of formation. Heat of formation of some compounds is

Compound	$\Delta H_f^{\circ},_{298}$ (kcal/kg mol)
Cu_2S	-18950
ZnS	-44000
FeS_2	-35500
FeS	-23100
CO_2	-94450
CO	-26840
Cu_2O	-42500
CuO	-38500
ZnO	- 83500
PbO	-52500

For example

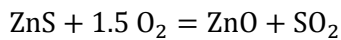


(c) is condensed and (g) is gaseous phase

This reaction produces heat at 298K

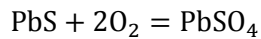
$$-\Delta H_R^{\circ} = 2 \times (\Delta H_f^{\circ})_{\text{CuO}} + (\Delta H_f^{\circ})_{\text{SO}_2} - (\Delta H_f^{\circ})_{\text{Cu}_2\text{S}}$$

$$-\Delta H_R^0 = 136990 \text{ k cal}$$



$$\Delta H_R^0 = (\Delta H_f^0)_{\text{ZnO}} + (\Delta H_f^0)_{\text{SO}_2} - \Delta H_f^0(\text{ZnS})$$

$$\Delta H_R^0 = -110440 \text{ k cal}$$



$$\Delta H_R^0 = -197000 \text{ kcal}$$

b) Combustion of fuel

In the ore concentrate solid fuel is mixed for roasting. Solid fuel contains carbon and hydrogen besides other elements. Fuel is characterized by calorific value. Gross calorific value of a solid fuel can be calculated by

Gross calorific value (kcal/kg) (GCV)

$$(\text{GCV}) = 81\%C + 341 \left(\% \text{ H} - \frac{\% \text{ O}}{8} \right) + 22\% \text{ S} .$$

If the coal analyses C 74%, H 6%, N1%, O9%, S 0.8% moisture 2.2% and ash 8%, GCV of coal is 32060 kJ/kg.

Determination of calorific value of gaseous fuel

In determination of gaseous fuel, combustible components are: CO, H₂, hydrocarbons, NH₃ etc., whereas O₂, CO₂, N₂ are diluents.

Heats of formation of some oxides are¹:

Oxides	$-\Delta H_f^0$ (1 atm, 298K)kcal/kgmol
CO	29.6×10^3 (C Amorphous)
CO	26.4×10^3
CO ₂	97.2×10^3 (C Amorphous)
CO ₂	94.05×10^3
H ₂ O(l)	68.32×10^3
H ₂ O(v)	57.80×10^3
SO ₂ (g)	70.96×10^3
SO ₃ (g)	94.45×10^3

Heats of formation of some hydrocarbons are:

Hydrocarbons	$-\Delta H_f^\circ$ (1 atm, 298K)kcal/kgmol
CH ₄	17.89x10 ³
C ₂ H ₂	-54.19x10 ³
C ₂ H ₄	-12.5x10 ³
C ₂ H ₆	20.24x10 ³
C ₃ H ₈	24.82x10 ³

To note

$$1 \text{ kgmol} = 22.4 \text{ m}^3 (1 \text{ atm}, 0^\circ\text{C})$$

$$1 \text{ kgmol} = 24.45 \text{ m}^3 (1 \text{ atm}, 25^\circ\text{C})$$

Consider an example of gaseous fuel of the following composition:

$$\text{CH}_4 = 4\%$$

$$\text{C}_2\text{H}_6 = 3\%$$

$$\text{C}_3\text{H}_8 = 0.5\%$$

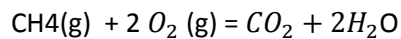
$$\text{N}_2 \text{ and } \text{CO}_2 = \text{Rest}$$

Let us calculate CV of this fuel

In 1 kg mole of gaseous fuel:

	Kg moles
CH ₄ =	0.94
C ₂ H ₆ =	0.03
C ₃ H ₈ =	0.005

Heat of combustion of Methane



$$\text{Heat of combustion} = (\text{Heat of formation of products}) - (\text{Heat of formation of reactants})$$

By substituting the values of heat of formation one obtains heat of combustion of methane equals $194.91 \times 10^3 \text{ k cal/kg mol}$.

Similarly, combustion equations for C₂H₆ and C₃H₈ can be written and heat of combustion value can be calculated.

Heat of combustion of $C_2H_6 = -350.56 \times 10^3$ k cal/kg mol and of C_3H_8 is -498.18×10^3 k cal/kg mol when reference state of POC is vapour. Thus net calorific value (NCV) of natural gas is

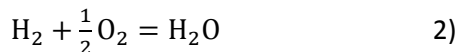
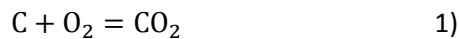
$$\begin{aligned} |\text{NCV}| &= 0.94 \times 194.91 \times 10^3 + 0.03 \times 350.56 \times 10^3 + 0.005 \times 498.18 \times 10^3 \\ &= 196.22 \times 10^3 \text{ k cal/kg mol of natural gas} \\ &= 8.76 \times 10^3 \text{ k cal/m}^3 \text{ (1 atm and 273K)} \end{aligned}$$

Amount of air

In roasting, air is used for oxidation of sulphides as well as for combustion of coal. Calculation of amount of air is important.

Stoichiometric amount of air (Also termed theoretical air or air for complete conversion of sulphide into oxide or for complete combustion) can be calculated by considering the products of combustion.

Consider the reaction



The equations 1 to 4 are chemically balanced equations. In equation 1, we require 1 mole of oxygen to produce 1 mole of CO_2 and in equation 3 or 4 we require 1.5 mol of SO_2 . It is known that 1 mole of oxygen is obtained from 4.76 moles of air.

Let us calculate stoichiometric amount of air for combustion of solid fuel of composition 84% C, 5% H, 5% moisture and 6% ash, per Kg of coal. Following the stoichiometry of combustion, the amount of air would be

$$\begin{aligned} \left(\frac{0.84}{12} + \frac{0.05}{2} \right) \times 4.76 &= 0.452 \frac{\text{moles}}{\text{kg}} \text{ coal} \\ &= 10.12 \text{ m}^3 \text{ (1 atm, 273K) / kg coal} \end{aligned}$$

Note 1 kg mole = 22.4 m³ (1 atm, 273 K)

$$\begin{aligned} \text{Excess air} &= \frac{\text{Actual amount of air} - \text{theoretical air}}{\text{theoretical air}} \times 100 \\ &= \frac{\text{actual amount of } O_2 - \text{theoretical } O_2}{\text{theoretical air } O_2} \times 100 \end{aligned}$$

In the above example if actual amount of air is 0.5 mols then

$$\text{Excess air} = \frac{0.5 - 0.452}{0.452} \times 100 = 10.62\%$$

We can also call that 110.62% theoretical air is used for combustion.

Similarly stoichiometric amount of air can be calculated for reaction 3 and 4. If reactions 3 and 4 occur simultaneously then stoichiometric amount of oxygen is 3 mols and stoichiometric air is 14.28 mols.

Types of roasting

In dead roasting all sulphides are converted into oxide. This is done to extract Zn from its sulphide ore.

In sulphatising roasting, sulphide is converted into sulphate as sulphate can be dissolved easily into an aqueous solution. Typically used for hydro metallurgical extraction of lead sulphide ores.

Conclusions

This lecture discusses roasting. Roasting is mainly used in production of copper, lead, zinc etc. In roasting sometime fuel is used. The calculation procedure for calorific value of solid fuel and gaseous fuel is illustrated through an example. Type of roasting presented here is in brief. Details can be seen in the references given below.

Reference:

- 1) Resenquist : principles of extractive metallurgy
- 2) H S Ray, R Sridhar and K.P Abraham: extraction of non ferrous metals.