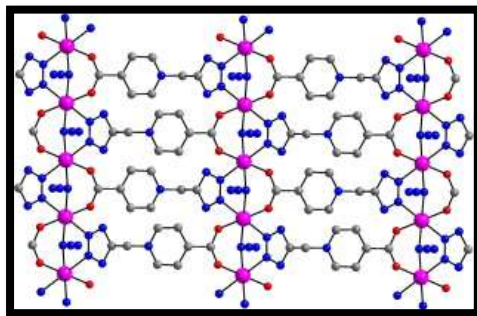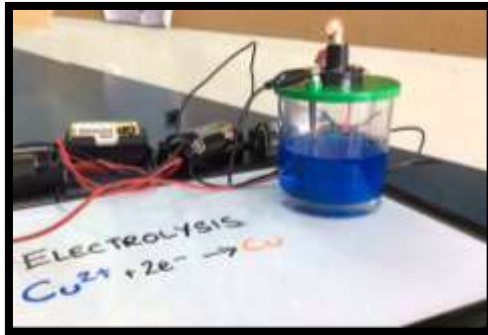**T.C.**
**YILDIZ TECHNICAL UNIVERSITY**

**FACULTY OF CHEMICAL AND METALLURGICAL ENGINEERING**

**METALLURGICAL AND MATERIALS ENGINEERING**
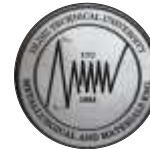


# MSE3961 LABORATORY-1 EXPERIMENT BOOKLET 2021-2022 FALL

# INDEX

## LABORATORY SAFETY INSTRUCTIONS

**1.** Handbags, coats, etc. should not be brought to the laboratory if possible. If these materials are brought to the laboratory, the materials should be kept at locations determined by the laboratory administrators.

**2.** During the application of laboratories, long hair should be tied up and pendant earrings and bracelets should be removed. If there are cuts, wounds, etc. on the hands, working in the laboratory is possible only after they have been covered with waterproof tape, peep toe shoes should not be worn in the laboratory.

**4.** Personal protective equipment (gloves, masks, eye / face protectors, hearing protection, work clothing) should be used to protect the eyes and the skin as long as worked in the laboratory.

**5**. No food and beverage should not be consumed in the laboratory, and the face should not be touched while working

**6.** It is necessary to know what is available in the first-aid chest and how the fire extinguisher works. Information about this must be obtained from the staff.

**7.** In the laboratory, movements that distract others should be avoided. Gaming or joking is strictly dangerous and forbidden in the laboratory.

**8**. Laboratory notebook should be kept for the studies conducted in the laboratory. Studies and observations must be recorded in this notebook.

**9**. Taps, gas valves and switches, should be kept closed when not in use.

**10.** Metallic laboratory tools should not be kept wet to avoid rusting.

**11**. The solid materials to be dispensed should be dropped into the designated waste bin in the laboratory.

**12**. Any incident occurred in the laboratory should be immediately notified to the administrators of the laboratory.

**13**. No substance or material should be taken out of the laboratory without the permission of the laboratory's administrators.

**14**. After use, each item should be cleaned according to the method of the appliance. Hands should be washed after leaving the laboratory.

**15**. Before using the microscope, the objective and ocular should be carefully cleaned with a cloth before and after each use without damaging the lens.

**16**. While diluting the acids and alkalis, they should always be poured slowly over the water, never the opposite.

**17.** If corrosive caustic substances such as acids or bases drip or splash to the naked skin, it should immediately be washed with plenty of water. The laboratory administrator must be informed about the incident.

**18.** When dealing with electricity, hands and electric switches and sockets must be dry. Electrical plugs should not be pulled out from the cord.

# 1. POWDER METALLURGY

**Purpose of Powder Metallurgy:** Metal and metal alloys are made a durable body with the help of pressure and temperature without melting their powder. This heat treatment, called sintering, replaces melting and is carried out at a temperature below the melting point of the metal powder used. In the sintering of single component powders, the sintering temperature can be lower than the melting temperature of the material (approx. 80% of the melting temperature). In multi-component systems, the sintering temperature can be selected from the components just below the melting temperature of the lowest melting temperature. This type of sintering is called solid phase sintering. In addition, sintering temperature in multi-component systems can be taken above the melting temperature of at least one of the components, such sintering processes are also called liquid phase sintering.

**Why Powder Metallurgy Manufacturing Method?**

The parts manufactured with T / M can be examined in two main groups depending on the preferred reason of this method.

**Group 1**: Parts of which the T / M method is more economical, although they can be manufactured by other methods.

**Group 2**: T / M's only alternative parts

**Powder Metallurgy Processes**
Powder metallurgy technique consists of 3 stages.
1. Powder production,
2. Pressing (powder particles into a single park with various operations),
3. Sintering and final parts production with secondary operations if necessary.


**PART 1.1: APPARENT DENSITY (WET DENSITY)**

**1.1.1 PURPOSE OF EXPERIMENT:** Determining the loose, uncompressed density of the powder and determining the conformity to the standards.

**1.1.2 TOOL, DEVICE AND MATERIALS USED:** Scale, metal powder, standard test apparatus

**1.1.3 THEORETICAL KNOWLEDGE AND EXPERIMENT:** The bulk density is the loose (uncompressed) density of the powder (g / cm$^3$). In order to determine this density, the size and shape of the powder is poured from a funnel specified in the standards and is provided to fill the cylindrical container with a free fall. The height between the funnel outlet and the upper surface of the cylindrical container is a constant value. Carefully peel off the excess powder in the cylindrical container which is filled and weigh the powder inside. Since the test container volume is known (25 cm$^3$), the bulk density is easily calculated as (g / cm$^3$). The ISO standard number of this experiment is 3923. All conditions and experiments were carried out. In Figure 1, the dimensions of the equipment used for this experiment are given schematically.

The apparent density of stainless steel powders produced by water atomization varies between 2.80-3.20 g / cm$^3$. This value can be up to 5 g / cm$^3$ for dusts produced by gas atomization. This value varies between 2.80-3.00 g / cm$^3$ for copper powders and 3.00-3.25 g / cm$^3$ for bronze powders. The bulk density is a very important factor in filling the mold of the powder during the pressing step. The bulk density is closely related to the shape, size and distribution of the powder grain. As the grain shape moves away from the sphere, the intergranular space rate decreases.
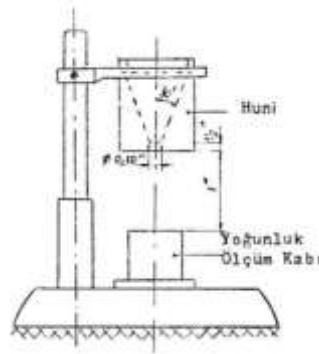


Figure 1.1 Measurement of Masonry Density

**PART 1.2: FLUIDITY TEST**

**1.2.1 PURPOSE OF EXPERIMENT:** Determination of the desired flow time from the powders and their compliance with the standards

**1.2.2 TOOL, DEVICE AND MATERIALS USED:** Scale, metal powder, standard test equipment, stopwatch

**1.2.3 THEORETICAL KNOWLEDGE AND EXPERIMENT**

The purpose of this test is to determine the fluency values of raw materials from X company. This rate is defined as the time that 50 grams of powder must pass through a 2.54 mm funnel. It has a flow time of 15 seconds for spherical stainless steel. This ratio varies from 25 to 30 seconds for irregularly shaped powders.

Fluency; the size and shape of a given amount of a powder type or mixture thereof is the ability to flow from a predetermined funnel. In these measurements, the flow time of the powder sample of 50 g of powder is generally determined and this value is considered as the flux of the powder. Funnel dimensions and shape with flow hole dimensions (hole diameter and length) are specified in the standards (ISO 4490). The experiment is usually repeated three times and the mean value is calculated. Its fluency also depends on the powder size, grain size, specific surface size and powder grain shape. Fluency increases as the grain size decreases.
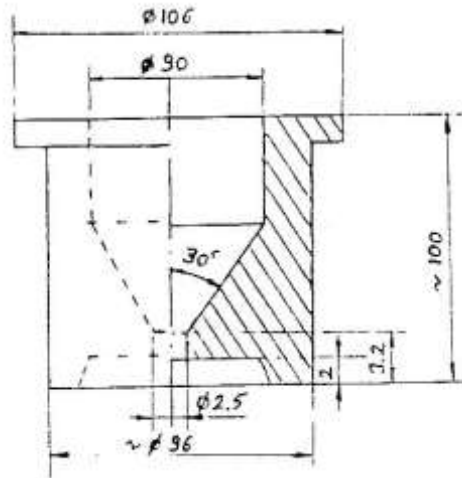
Figure 1.2 An Experimental Funnel for Determining Fluency is Shown Schematically.

## PART 1.3: COMPRESSIBILITY (GREEN DENSITY)

**1.3.1 PURPOSE OF EXPERIMENT:** Determination of the theoretical density of the powder after pressing.

**1.3.2 TOOL, DEVICE AND MATERIALS USED:** Scales, metal powder, press, caliper, mold.

## 1.3.3. THEORETICAL KNOWLEDGE AND EXPERIMENT

This property corresponds to the density obtained when the powder is under pressure. This is the density reached after pressing. Austenitic stainless steel powders have better compressibility than martensite. compressibility; The yield limit is a function of the sample's hardness, the softness of the particles, the void ratio of the sample, the shape and size of the grains.

If the metal powders are formed in the mold, it is provided that the powder free to fill the mold cavity very well and fully (high fluency capability) as close to the theoretical density as when it is pressed into the mold cold (when stapled).

The softer the material, the higher its compressibility. The compressibility is also closely related to the friction between the beads and the molds in the pressing of the powder grains. The theoretical density of the component: for example, the green density obtained for Fe is 6.65 g / cm 3, Fe: 7.87 g / cm 3: (6.65: 7.87) * 100 = 84.5% = % theoretical density.

- 84,5% Filled
- 15.5% Pore

## PART 1.4: SIEVE ANALYSIS, DIMENSIONAL DISTRIBUTION AND CALCULATION OF AVERAGE PARTICLE SIZE

**1.4.1 PURPOSE OF EXPERIMENT: Classification of powder particles of different sizes according to their size and calculation of average powder particle size.**

**1.4.2 TOOL, DEVICE AND MATERIALS USED**: Metal powder, sieves, scales with different apertures.

**1.4.3 THEORETICAL KNOWLEDGE AND EXPERIMENT**

The calculation of the distribution of certain particles of powder according to the shape and weight of the grain particles. In this method, the top layer of the sieves, which are lined up from the top) to the top of the bottom, are put on dry weight (weighing 100 or 50 grams) of metal powder and vibrated for a period of time on each sieve. The grains are weighed precisely. A table is organized as follows. The screens must be anti-magnetic.

Table 1.1 Sieve Analysis Chart (example

| Aperture size<br>d<br>(μm) | Oversize<br>ΔR<br>(% volume) | Residue on sieve<br>R (%) | Undersize powder amount<br>D(%) | Average grain size for each sieve<br>da (μm) |
|---|---|---|---|---|
| 0.400 | 0 | 0 | 100 | 0.45 |
| 0.315 | 5.5 | 5.5 | 94.5 | 0.36 |
| 0.200 | 20.5 | 26.0 | 74.0 | 0.26 |
| 0.100 | 42.0 | 68.0 | 32.0 | 0.15 |
| 0.063 | 23.0 | 91.0 | 9.0 | 0.08 |
| 0.040 | 6.6 | 97.6 | 2.4 | 0.05 |
| 0.040 | 2.4 | 100.0 | 0.0 | 0.02 |

The values in this table:        $d_o = \Sigma \Delta R * da / 100$

  $d_o$: Arithmetic mean grain diameter
  %R: Quantity on each sieve,%
  R: Sum of sieve size,%
  da: average grain size for each sieve, mm
  D: Amount passed through the screen,%

Example:

$d_o$=(0 * 0.045) +(5.5 * 0.36) + (20.5 * 0.26) + (42 * 0.15) + (23 * 0.08) + (6.6 * 0.05) +     (2.2 * 0.02) / 100= 0.136 μm.

## PART 1.5: COMPRESSING

**1.5.1 PURPOSE OF EXPERIMENT:** Determination of pressure-density relationship for different pressures by shaping powders in molds

**1.5.2 TOOL, DEVICE AND MATERIALS USED**: Metal powder, mold, press

**1.5.3 THEORETICAL KNOWLEDGE AND EXPERIMENT**

Densification in Powder Metallurgy is the second important process. Pressing is that prepared metal powder mixture is compressed to reach the predetermined density in the appropriate press. It forms the metal powder filled into the press mold into a solid object. In order to achieve a high degree of pressing, a well-formed powder and high pressing pressures are required. The density achieved by pressing affects the mechanical properties of

The parts produced by powder metallurgy in the first degree.
Pressing is mostly cold (room temperature), but in special cases it is also hot. By pressing, the metal powder is given a desired level of density and mechanical strength according to the size and shape of the piece to be produced.
There are three basic steps in the mold condensation process.
1. Fill the mold cavity with the specified amount of metal powder,
2. Compression of the powder by means of staples,
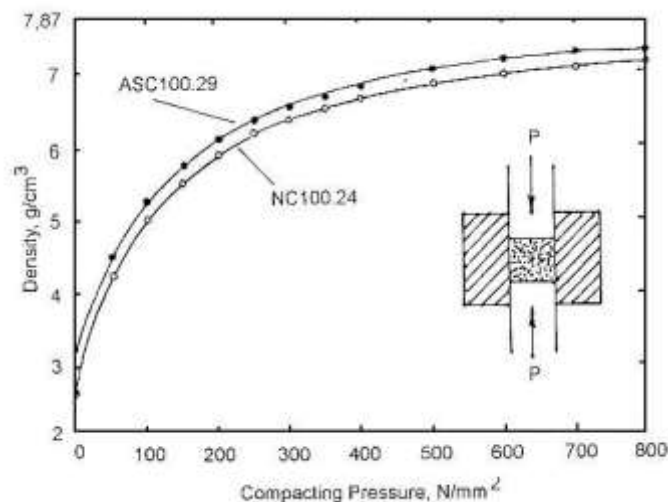3. Removing the shaped part from the mold.



Figure 1.3 Density-pressure relationship for two commercial iron powders

\* pressure ↑   ,   density ↑,   pore ↓

\* pore ↑,   density ↓

\* pore ↑,   strength  ↓

\* pore ↑,   lubricant ability   ↑

**Porosity:** Sintered bushing, oil pump rotor, gears, bearing material etc. used in places. (After the production of the parts is completed, the powders in the pore are vacuumed, oil is given under vacuum, air is taken from the pores and oil is pumped into the cavities).

## PART 1.6: SINTERING PROCESSES APPLIED TO METAL POWDERS

**1.6.1 PURPOSE OF EXPERIMENT:** Effect of sintering process conditions on structure and properties

**1.6.2 TOOL, DEVICE AND MATERIALS USED:** T / M sample, atmosphere controlled oven.

**1.6.3 THEORETICAL KNOWLEDGE AND EXPERIMENT**

Sintering is the heat treatment applied on the powder without disrupting the shape of material. Prestige shaped powder is not suitable for use in this form. However, the required strength increases with sintering. In this process, diffusion occurs between the powder grains at certain temperature and time, and weak mechanical bonds become strong mechanical bonds. Sintering temperature and time; A suitable sintering temperature and time should be determined according to properties desired for the parts. The main reason for the low density and strength in the parts is the very low sintering temperature and time. The sintering temperature should be as close as possible to the melting temperature of the powder.

Table 1.2 Sintering temperature and time of some metals and alloys

| Powder materials | Sintering temperaturee (ºC) | Sintering Temperature Standby Time (min) |
|---|---|---|
| bronzes | 760-871¬820 | 10-20 |
| Brasses | 843-898 | 10-45 |
| copper | 843-898 | 12-45 |
| Steel, C' steel | 1010-1148 | 8-45 |
| Stainless steels | 1033-1287 | 30-60 |
| Fe (ferrit) | 1204-1482 | 10-600 |
| nickel | 1010-1148 | 30-45 |
| Alnico magnets | 1204-1301 | 120-150 |
| Tungsten Carbides | 1426-1482 | 20-30 |
| Molybdenum | 2054 | 120 |
| Tungsten | 2343 | 480 |

**REFERENCES:**

- Toz Metalürjisi Ders Notları, Adem BAKKALOĞLU, 2015.

- Toz Metalürjisi ve Parçacıklı Malzeme İşlemleri, Randall M. GERMAN, 2007

- Höganas Handbook For Sintered Components, 1997.

- Powder Metallurgy Science, Randall M. GERMAN, 1994.

- ASM Handbook Volume 7, Powder Metallurgy, 1993.

## 2. PRECIPITATION HARDENING

**2.1 AIM:**

The objective of this laboratory is for you to explore the strengthening of Al by precipitation hardening.

To increase the hardness of the material by the thermal process without changing the chemical composition.

**2.2 THEORY:**

Pure FCC metals such as Al have low yield strengths because the stress required to move a dislocation is small. One method of strengthening an alloy is through precipitation reactions. "Precipitation hardening" is the process of hardening or strengthening of an alloy by precipitating finely dispersed precipitates of the solute in a supersaturated matrix. This process involves the following three basic steps:

1. The first step is the solution heat treatment or homogenization. Figure 9.1 illustrates this phenomenon. During this step, an alloy of composition X1 is heated to a temperature T1, between the solvus and solidus temperatures and soaked there until all of the solute dissolves into the α phase and a uniform solid-solution structure is produced.

2. The second step is quenching. Quenching is simply cooling the sample rapidly to a lower temperature, T3, usually room temperature, and the cooling medium is usually water at room temperature. During quenching, the solute is not immediately able to diffuse out of a phase and the alloy is said to be supersaturated. The rationale behind the quenching process is to preserve the uniform solid solution structure of the alloy below the homogenization temperature.

3. The final step in the precipitation hardening process is aging. It is the process of precipitating incoherent precipitates from a supersaturated solid solution. When aging occurs at room temperature, it is called "natural aging". Aging above room temperature is called "artificial aging".
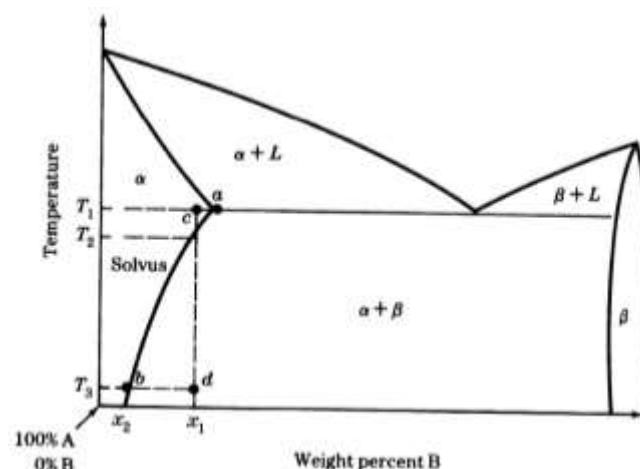


**Figure 2.1** Binary phase diagram for two metals A and B having a terminal solid solution which has a decreasing solid solubility of B in A with decreasing temperature

The phase diagram for Al-Cu is illustrated in Figure 2.2. By solution annealing an Al alloy (2024) containing ≈4.4 Wt% Cu, and then quenching, i.e. cooling so fast that little diffusion is possible, the Cu can remain dissolved in Al, but it is not in equilibrium. It was mentioned above that solute hardening is not an effective hardening mechanism, and so the quenched alloy must be slowly annealed to precipitate incoherent $Al_2Cu$ (θ phase) particles. Since the number density of precipitates controls hardness, not the size of the individual particles, the trick is to nucleate as many particles as possible but keep them from growing. If the anneal is too long or at too high a temperature, some precipitates will grow while others shrink and disappear, lowering the number of precipitates and the strength. This condition is called overaging.
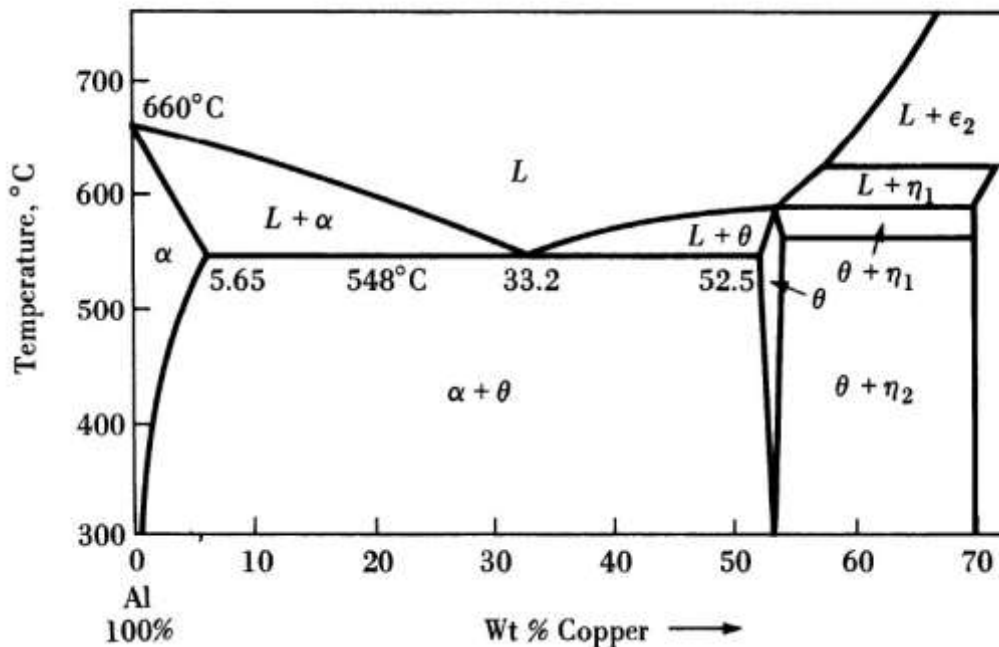


**Figure 2.2** Phase diagram for Al-Cu

As it turns out, Cu in aluminum do not simply precipitate out according to the phase diagram, but rather it forms metastable precipitate phase, before finally forming the equilibrium phase, such as $Al_2Cu$. For Al-Cu, the first phase to form is a fully coherent precipitate called a GP (Guinier Preston) zone. This is followed by intermediate θ" and θ' phases before the stable θ ($Al_2Cu$) phase forms. As these reactions occur, the hardness changes, at first increasing as the precipitates nucleate and grow (or age), and changing from coherent to incoherent phases. Eventually the strength decreases as the incoherent precipitates grow in size but decrease in number (i.e., overage), given in Figure 2.3.
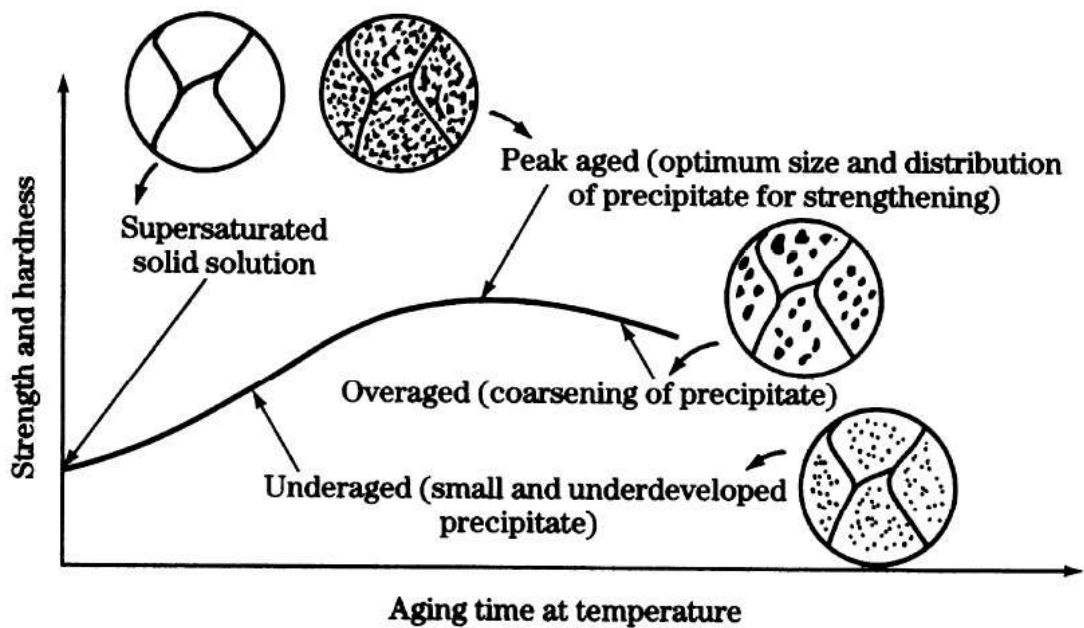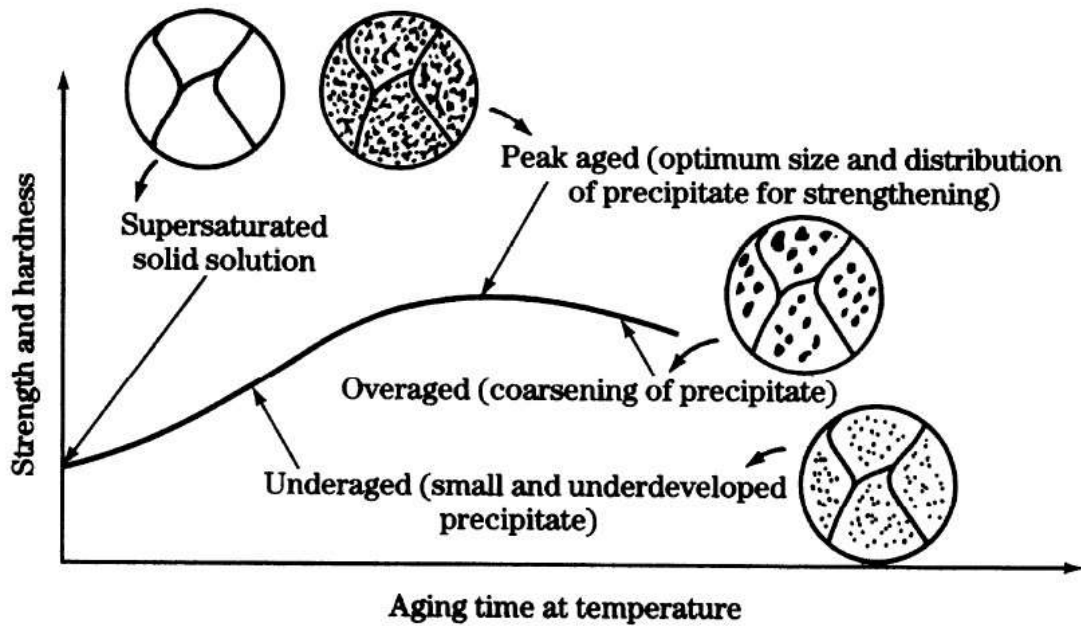
**Figure 2.3** Microstructural development with aging time.

## 2.3 STANDARTS

ASTM: B918/B918M

## MATERIALS AND APPARATUS

- Heat treatable Al samples
- Heat treatment furnace
- Quenching gadget
- Oven
- Hardness test machine

## 2.4 PROCEDURE:

Two types of heat treatments will be conducted:

1. Temper T4: Solution treatment and water quench and natural aging.

2. Temper T6: Solution treatment, water quench, and artificial aging.

In this experiment heat treatable Al alloy such as AlMgSi or AlCuMg will be used. All specimens must have at least 2 mm thickness. Commercially purchased Al alloys should be solutionized and quenched into cold water. In this lab, we will use a common solutionizing time of 30 min. and a solutionizing temperature of 520-530 ℃. For temper T4 hardness measurement must be made immedaitely cause precipitation process begins at the time. For temper T6, the bars should be aged at 150 C for ½, 1, 2, 3, 4, 5, 6, 8, 10 h and 200 C and 250 C degrees for ¼, ¾, 1,5, 2,5, 3,5, 5  h, following the solutionizing and water quench. After the aging, the samples should be removed and allowed to cool in air.

## 2.5 PRECAUTIONS

- Proper solution time must be given to the specimens.
- Proper care should be taken while hardening the specimens.
- The specimens must be as per IS and BS specifications.

## 2.6 STUDENTS PREPARATION PRE- AND AFTER EXPERIMENT

Pre-experiment; Students are to be research and study about chemical compositon of Al alloys, and its effect on the hardening mechanism, Precipitation Hardening mechanism and heat treatment conditions of given materials.

After experiment; Students are to do hardness test after tempering on the Al samples. All hardness values versus time are to be shown as graphic style and the reason of differences between these values are to be explained.

Experiment report shall include;

- Description Precipitation Hardening of metallic materials

- Main theme of test

- Used materials, equipments and apparatus of experiment,

- Test conditions

- Hardness values obtained from experiment are shown as graphical style

- Detailed analysis of differences between samples

- References

## 3. CORROSION EXPERIMENTS

### PART 3.1: CORROSION OF ZINC IN ACIDIC SOLUTION

**3.1.1 AIM:** Investigation of the electrochemical behavior of zinc in acidic solution.

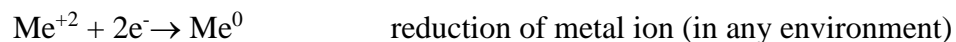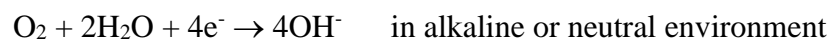### 3.1.2 THEORIC INFORMATION

Electrochemical corrosion is the degradation of metals in aqueous environments. There is no need for external energy in electrochemical corrosion that occurs spontaneously with the formation of electrochemical cells in the metal-media system.

In order for electrochemical corrosion to occur, there must be 5 elements in the system. These; anode, cathode, interface, electronic conductor and electrolytic conductor. During electrochemical corrosion, while oxidation reaction is observed at the anode, different reduction reactions occur at the cathode depending on the pH of the environment. The reactions that take place are as follows:

On anode;

$$Me^0 \rightarrow Me^{+2} + 2e^-$$

On cathode;

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{in acidic environment}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad \text{in acidic environment}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad \text{in alkaline or neutral environment}$$

$$Me^{+2} + 2e^- \rightarrow Me^0 \qquad \text{reduction of metal ion (in any environment)}$$

Corrosion occurs at the anode sites. On the other hand, cathodic reactions take place at the cathode, and degradation does not occur in these regions of the metal.

There are various methods for the quantitative evaluation of the corrosion experiments. In the Various methods are used for the quantitative evaluation of corrosion tests. In the mass loss method, the test sample is weighed before and after the test, and the resulting weight loss is calculated. Then, the corrosion rate is calculated with the help of the formula below.

$$H = K \cdot \Delta G / A \cdot d \cdot t$$

H: corrosion rate

K: constant for the desired corrosion rate unit ($3.45 \times 10^6$ for mpy)

G: weight loss (gr) ($\Delta G = G_1 - G_2$)

A: surface area exposed to the solution ($cm^2$)

d: metal density ($gr/cm^3$)

t: duration of experiment (sn)

The fact that the cathodic reactions in electrochemical corrosion phenomena is hydrogen and oxygen reduction, in some cases, allows the determination of the amount of gas released during the experiment and the determination of the corrosion rate. At very low rates of corrosion, calculating the increase of the metal ion concentration in the corrosive solution gives more accurate results than calculating the weight loss in the metal sample. In determining the corrosion rate, a suitable method, that will give an accurate result, should be chosen.

### 3.1.3 EXPERIMENTAL PROCEDURES

**Equipment and Materials:** Beaker, glass funnel, burette, pipette pump, drying machine, scales, waterproof polishing papers, HCl solution, zinc, rope.

**Experimental:**

Zinc sample is cut in a certain size from the zinc plate and make a hole to hang. And then the surface and edges of the sample are polished using water proof abrasive papers having various grit numbers following by cleaned from the oil and dirt on the surface in the ultrasonic bath. The sample, whose dimensions and weight are measured, is fixed to the bottom of the funnel using the line rope. The funnel is placed through a burette and is put it upside down in a beaker filled with the HCl solution of pH 1, as shown in Figure 1. And the the solution is drawn into the burette at a certain level. The drop in the solution level is recorded every 3 minutes. When the solution level in the burette reaches zero, the experiment is terminated and the time is recorded. At the end of the experiment, the sample is removed from the solution, washed, dried and weighed again.
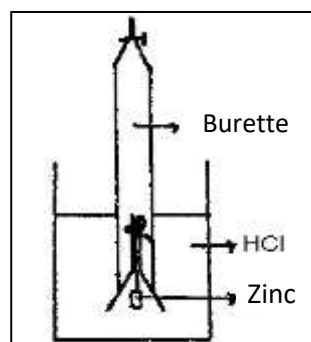


Figure 3.1 Experimental set-up

### 3.1.4 REQUIREMENTS:

1. Write cathodic and anodic reactions.

2. Calculate the total corrosion rate (mpy) using the method of the calculating the mass loss.

3. Calculate the total corrosion rate (mpy) using the method of the determining the amount of the evolved gas during the test. Plot the change in corrosion rate depending on the time, using

the dissolved amount of zinc (mgr) -time (min) axes and examine this change and find the corrosion rate. Use the recorded your gas volume readings in the burette during experiments.

4. Compare the corrosion rates calculated using both the methods of the calculating the mass loss of the samples and the determining the amount of the evolved gas during the test. Is the corrosion rate determined by the weight loss the same as the rate of corrosion determined by the loss of hydrogen gas? If not, indicate the reasons.

## PART 3.2: GALVANIC CORROSION

**3.2.1 AIM:** Determination of the effect of cathode / anode surface areas and stirring of solution on corrosion rate in galvanic corrosion.

### 3.2.2 THEORIC INFORMATION

The potential difference in any system can be caused by many reasons:

- Contact of different metals,
- Difference in ion concentration on the metal surface in the solution,
- Different stress zones in metal,
- Internal structure differences in metal,
- Temperature differences.

Galvanic corrosion is a type of corrosion that occurs when different types of metals and alloys in contact with each other are placed to the same atmosphere. While the metal, which has a more negative electrode potential than the other metal which is into contact with each other, is acting as an anode and degrades, the other metal acting as a cathode and protected from corrosion. As the potential difference between the metals increases, the probability of galvanic corrosion increases. The environmental mobility and the surface size of the metals are also important among the other factors affecting the galvanic corrosion. In case of the active metal has a smaller surface area than the noble metal, the corrosion is faster because a small anode area raises electrons to a larger cathode area.

### 3.2.3 EXPERIMENTAL PROCEDURES

**Equipment and Materials:** Beaker, magnetic stirrer, ultrasonic cleaner, 1Ω resistor, 2 electrode holders, multimeter, steel and copper plates, various waterproof abrasive paper, 3.5% NaCl solution, methyl alcohol.

**Experimental:**

In this experiment, copper and steel pairs are used. First, the surfaces of the samples are cleaned, washed and removed oil. Then the parts, which will be dipped into the solution, are marked on the surfaces. First, copper and steel sheets having equal size are placed in electrode holders and immersed in 3.5% NaCl solution (Figure 2). The current flowing is recorded through a resistor connected between the electrodes through the system after waiting for 3 minutes. And then the solution is started to stir and the current is again recorded after 3 minutes. The abovementioned procedures are repeated using large copper-small steel and small copper-large steel plates.
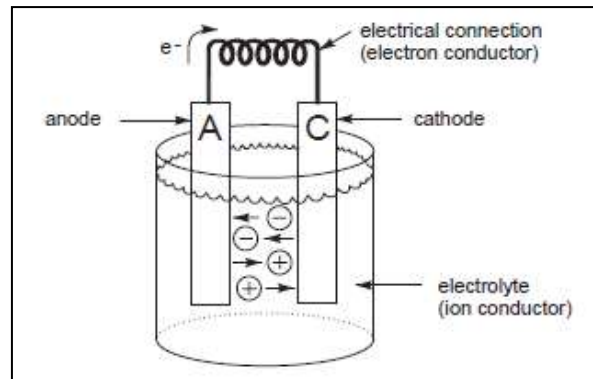
**Figure 3.2** Experimental set-up in galvanic corrosion

### 3.2.4 REQUIREMENTS:

1. Define and write each anodic and cathodic reactions.
2. Draw the relation of $A_{anode}$ / $A_{cathode}$ as a graph for all measurements (steady and stirred state) and explain.

## 4. CARBOTHERMIC REDUCTION

### 4.1 OBJECTIVE OF THE EXPERIMENT

The objective of this experiment is to investigate the thermodynamic and kinetic aspects of the solid state reduction of ferrous raw materials using carbon (carbothermic reduction).

### 4.2 THEORETICAL INFORMATION

The iron and steel industry is a sector that produces products with the desired chemical and physical properties by melting iron ore in blast furnaces or scrap in arc furnaces. The finished steel products have numerous types and uses. Changing consumer needs, developments in technology and competition are further increasing the product diversity in the iron and steel industry. The most important heavy industry, iron and steel industry, provides raw materials to many significant industries like construction, infrastructure, automotive, white goods and industrial machinery industries. Therefore, the industrialization of a country is directly related to its strong iron-steel industry and consumption [1-3].

Two different methods are used for production of iron and steel products. These are production in integrated plants from ore and production in electric arc furnace plants from scrap. In integrated plants, the iron and steel production process begins with the preparation of iron ore by sintering or pelletizing, or charging the iron ore directly to the blast furnace. In blast furnaces, the ore is reduced with the aid of coke, and liquid iron is obtained. The resulting liquid pig iron is converted to steel in a basic oxygen converters. In the electric arc furnace, the steel scrap is melted in the arc furnaces and the desired chemical composition is obtained [4-6].

China, Japan and U.S.A. are the iron and steel top producers around the world. Nearly half of the world's iron and steel production is carried out by China. Turkey ranks 8th in the world with a share of 2.08% in iron and steel production and second in Europe. According to 2014 data, 10,283 million tons of 34,035 million tons of crude steel produced in Turkey is equivalent to 30,21% of the total amount of raw steel produced in our country, while 23,752 million tons corresponding to 69,79% are produced by 28 electric arc furnaces [1-3].

Iron is most abundant in the form of oxides as hematite ($Fe_2O_3$) and magnetite ($Fe_3O_4$). Removal of oxygen from the structure of oxides and transforming it to their lower oxides and/or metallic phase by using reductants ($CO$, $H_2$, $C$), which have higher affinity to oxygen, is called reduction.

Reduction of iron oxides is conducted technologically by two different methods. The first method is the indirect reduction with CO gas resulting from the reaction of coke combustion ($CO_2$ formation), and reduction of $CO_2$ by carbon in accordance with Boudouard Reaction, in the blast furnace, which is the first stage of steel production in integrated plants and where liquid pig iron production is performed (indirect reduction). A part of the reduction takes place in the lower zones of the blast furnace directly by solid carbon (direct reduction). The temperature in the blast furnace tuyere zone is up to 2000 ºC and the resulting product is liquid crude iron (pig iron). A modern blast furnace produces over 10,000 tons of liquid crude iron per day [4-6].

The other reduction method is a process in which iron oxides are converted to solid metallic phase without melting by solid or gas reducing agents. This method, known as direct reduction, produces sponge iron (Direct Reduced Iron) with high metallization ratio. Due to its low trace element and composition stability, sponge iron is an alternative to high quality steel in electric arc furnaces for high value added products. This method is not as widespread as blast furnaces, but has industrial importance. In 2014, 74.6 million tons of sponge iron were produced in the world. Today, MIDREX and HYL / Energiron processes, that use gas reducers, are the most common sponge iron production methods. The SL / RN process is the most common of all coal-using plants [7,8].

Sponge iron is the name of the product, which is produced by reduction of granulated, lump or pelletized iron ore with using gas or solid reducing agents under its melting temperature (950 ºC - 1100 ºC). The obtained product contains high metallic iron as well as gangue components from ore, unreduced iron oxides and some carbon. The sponge iron has the following properties;

- total iron content generally over 85%,

- the degree of metallization varies between 90% and 95%,

- carbon content is between 1 and 2.5%,

- gang content varies between 2-4%,

- the sulfur content is less than 0.005% for sulfur-free gas processing and 0.02% for processes using sulfur-containing coal and limestone,

- apparent density ≤4 g/cm$^3$.

To allow the sponge iron to be stored under ambient conditions and to be easily charged to the arc furnace, HBI (Hot Briquetted Iron) is produced by compressing pellet and lump of sponge iron under high pressure at a temperature of more than 650 ºC [9].

The fact that most of the production in our country is conducted by electric arc furnace plants which use high amount of scrap as raw material and the scrap amount in our country is much lower than the usage, makes the country dependent on foreign supplies. The Turkish iron and steel industry supplies 30% of the scrap used as raw material in the arc furnaces from domestic sources and 70% from imports. Also 40% of the iron ore, which is the raw material needed by the integrated facilities, is supplied by domestic and 60% by import. In 2013, 19.7 million tons of iron and steel scrap were imported. According to ITC-Trade Map statistics; Turkey, which is the world's largest iron and steel scrap importer in 2010, achieves 16% of world scrap imports [8].

In order to eliminate the dependence on external scrap, examination of alternative technologies which produces steel from iron ore is required. Some other factors in the emergence of alternative iron and steel technologies are:

- reduction of raw material cost,

- increasing of productivity by reducing product cost,

- enhancing of product quality,

- new product development,

- energy-saving,

- Increasing of recycling,

- solution of environmental problems.

The basis of alternative iron steel production is the production of sponge iron from iron ore by solid pre-reduction, which consists of low-temperature reaction at the top of the blast furnace [9].

Iron ore pellets are frequently used as raw material in sponge iron production. Iron ore pellets are industrial charging materials obtained as fine-grained minerals rich in iron by agglomeration and induration. The iron pellet has higher cost than other charge elements (lump iron ore and sinter). Despite this disadvantage, it is one of the indispensable inputs of the blast furnace thanks to its features. The reasons why the pellets are near ideal for the blast furnace can be summarized as follows:

- high iron content (65-67% Fe),

- superior resistance to crumbling and dusting due to its high strength and transport properties,

- good gas permeability due to their close size and uniform gas distribution,

- good reducibility properties due to high porosity.

Providing the desired characteristics ensures that positive results such as the use of high-temperature pellets, reduction of coke consumption, reduction of the amount of slag, increase of production speed are achieved [9].

**Thermodynamic Investigation of Reduction Reaction**

The carbothermic reduction of iron oxides to metallic iron, is accomplished by removal of the oxygen contained in the raw materials by deterioration of the iron-oxygen-carbon thermodynamic equilibrium to the reduction condition. In this condition, iron oxides reduce to metallic iron by the result of series reactions [4-6].

The reduction of the iron oxide in blast furnace is carried out by reductive CO gas, which is obtained by re-reacting of $CO_2$ gas with carbon, due to the fact that $CO_2$ gas, produced by combustion of carbon, is unstable at high temperatures (see Ellingham Diagram).

$$C_{(k)} + O_{2\,(g)} = CO_{2\,(g)} \tag{1}$$

$$CO_{2\,(g)} + C_{(k)} = 2CO_{(g)} \quad \text{(Boudouard Reaction)} \tag{2}$$
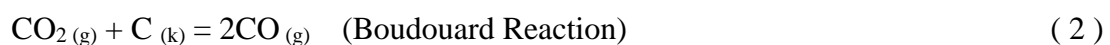
The reduction of hematite to iron with $CO/CO_2$ gas mixture, takes place in three stages. The temperature-dependent empirical expressions (3), (4), and (5) of the standard free energy change ($\Delta G°T$) for these reactions and reactions are given below.

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \qquad \Delta G^o_T = 4.376.000 + 1454,91\ T \qquad (3)$$

$$Fe_3O_4 + CO = 3FeO + CO_2 \qquad \Delta G^o_T = 1.610.900 - 27.54\ T \qquad (4)$$

$$FeO + CO = Fe + CO_2 \qquad \Delta G^o_T = -18.700 + 22,46\ T \qquad (5)$$

In order to determine the reduction conditions of iron oxides, firstly the equilibrium conditions must be determined with the help of the following relations.

$$\Delta G_T = 0\ \text{(Equilibrium Condition)} \qquad (6)$$

$$\Delta G^o_T = -RT\ln K_p \qquad (7)$$

$$K_p = \frac{a^2_{Fe_3O_4} \cdot P_{CO_2}}{a^3_{Fe_2O_3} \cdot P_{CO}} \qquad (8)$$

When $Fe_3O_4$ and $Fe_2O_3$ are assumed to be pure, their activities are equal to "1". In this case;

$$\Delta G^o_T = -RT\ln\frac{P_{CO_2}}{P_{CO}} = RT\ln\frac{P_{CO}}{P_{CO_2}} \qquad (9)$$

From this, the $\left(\dfrac{P_{CO}}{P_{CO_2}}\right)_D$ ratio which balances the reduction reactions at the $T_1$ temperature can be calculated. The basic thermodynamic condition for the reduction of iron oxides is as follows for each reaction.

$$\Delta G_T < 0 \qquad (10)$$

$$\left(\frac{P_{CO}}{P_{CO_2}}\right)_{Ortam} > \left(\frac{P_{CO}}{P_{CO_2}}\right)_{Denge} \qquad (11)$$

The Baur-Glaessner diagram and Boudouard curves drawn using reactions (2) and (9) are shown in Figure 1.
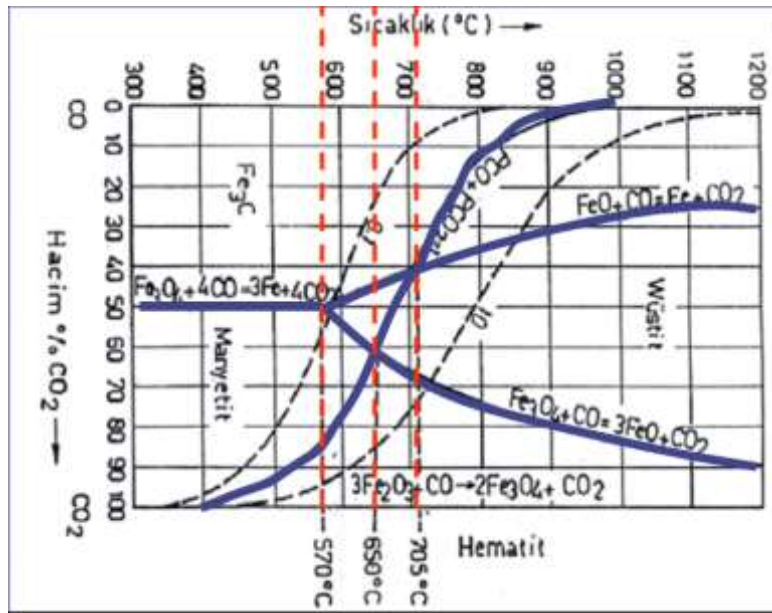
**Figure 4.1** Bauer-Glaessner diagram and Boudouard curves

According to Figure 1, the metallic iron reduction of iron oxides at a total pressure of $P_{CO}$ + $P_{CO_2}$ = 1 atm is only possible above 705 °C, under 705 °C, hematite to magnetite and magnetite to wustite transformation is possible. It can be seen from Figure 1 that a magnetite-wüstit transformation occurs between 650 and 705 °C and a hematite-magnetite transformation occurs below 650 °C. It can be seen that as the total pressure of $P_{CO}$ + $P_{CO_2}$ increases, the reduction temperature of the iron oxides is forced to shift to higher temperatures [4-6].

**Kinetic Analysis of Reduction Reaction**

In a reaction, the reaction rate can be determined by the time-dependent change in the quantitative properties of a substance participating in the reaction. Accordingly, the reaction rate can be given by;

$$r = -\frac{dC}{dt} \qquad (12)$$

The reaction rate can be calculated from the slope of the change in concentration plotted against time. The most important parameters affecting the rate of a homogeneous reaction are temperature and concentration.

k = reaction rate constant (temperature dependent)

$$r = -\frac{dC}{dt} = kC^n \qquad \text{C = concentration} \qquad (13)$$

n = reaction ratio

One of the most important parameters affecting the rate of chemical reactions is temperature. The equation for obtaining the relation between temperature and velocity constant in homogenous reactions is Arrhenius equation.

$$k = A.e^{-EA/RT} \qquad\qquad (14)$$

In this equation, $E_A$ is the activation energy. The rate constants k must be determined for at least two temperatures to determine the activation energy. A is the frequency (frequency) factor and R is gas constant (R= 8.314 J/mol K). As seen from the Arrhenius equation, the reaction rate depends on the temperature as an exponential function. A small change in temperature increases the rate constant drastically. Taking the logarithm of both sides, the following relation equation is obtained.

$$\ln k = \ln A - \frac{E_A}{RT} \qquad\qquad (15)$$

To calculate the activation energy, when the graph of ln k - 1/T is plotted, the angle of the line obtained is equal to the slope ($-E_A$ / R) (Figure 2).
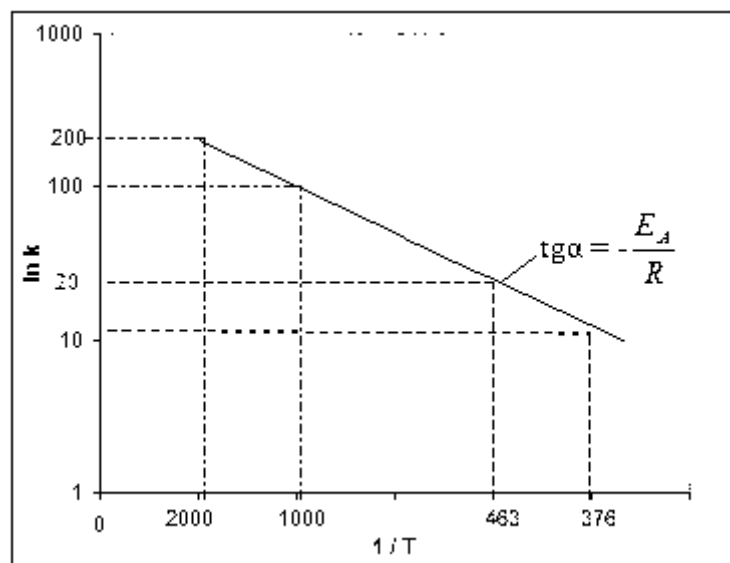


**Figure 4.2** Change of reaction rate with temperature

Reactions are termed as homogeneous and heterogeneous reactions, respectively, according to their occurrence between one or more phases. The reduction of iron oxide raw materials is a heterogeneous reaction. Heterogeneous reactions occur between more than one phase and are characterized by the presence of an interface between the reactants. For example, in the case of a solid-gas reaction, the interface layer is the outer surface of solid, which is in contact with the gas. In this case, we can gather all heterogeneous reactions in five groups depending on their interface: Solid-Gas, Solid-Liquid, Solid-Solid, Gas-Liquid, Liquid-Liquid [10-13].

The occurrence of heterogeneous reactions between more than one phase is as follows [10,11]:

1. Transport of the reducing gas to the reaction interface (diffusion)

2. Interfacial reactions.

    a) Adsorption of the reducing gas to the reaction interface.

    b) Chemical reaction at the interface.

    c) Desorption of the products occurred after the reaction.

3. Interfacial transport of reaction products resulting from reaction (diffusion)

Generally, the rate constant of one of the steps listed above is very low compared to the others. In this case, this step is the step controlling the rate, and the rate of this step determines the total reaction rate. Heterogeneous reactions develop, depending on the slowest step:

- **Diffusion Controlled**

- **Chemical Reaction Controlled**

If the rate constants of these two steps are equal;

- **Mixed Controlled**

The interfacial area in heterogeneous reactions is of great importance as the amount of material carried in transferring the reactants from one phase to the other depends on the interface area. In reactions with solids, small grained solids react faster than large grains due to their larger surface area [10-13].

The geometric shape of the solid material entering the reaction with liquid or gas plays an important role in determining the rate of the relevant reactions. If the solid is disc or plate-shaped, it is assumed that the surface area remains constant throughout the reaction. Because the reaction on the disc and the plate proceeds from surface towards the interior by protecting the surface area of the surface. However, if the solid is spherical or pellet-shaped, the reaction proceeds inward from the outer surface of the sphere. In this case, as the diameter of the reaction surface is reduced, the surface area changes continuously throughout the reaction and therefore the reaction rate decreases. Since the solids reacting is generally regarded as a sphere, the relationship between the rate constant for the chemical reaction in the heterogeneous reaction and the realization rate of the reaction is given as:

$$1-(1-R)^{1/3} = kt \qquad (16)$$

*R = Realization rate of reaction )can be indicated by letters n, x, F, L)*

*$W_o$ = İnitial weight*

$$R = \frac{W - W_o}{W_o} \qquad (17)$$

*W = Final weight*

The reaction interface of spherical solid materials is quite evident. As the reaction progresses, the reaction interface travels from the outer surface to the center of the particle, and there is a definite boundary between the unreacted area and the reaction surface. This model reaction is called the topochemical model or the shrinking core (Figure 3).

If the reaction products formed are dissolved in the environmental phase, the surface area will decrease over time. Typical examples of this are combustion of coke or dissolution of a solid in a liquid. In this reaction model, the step controlling the reaction rate will be chemical reaction or diffusion.
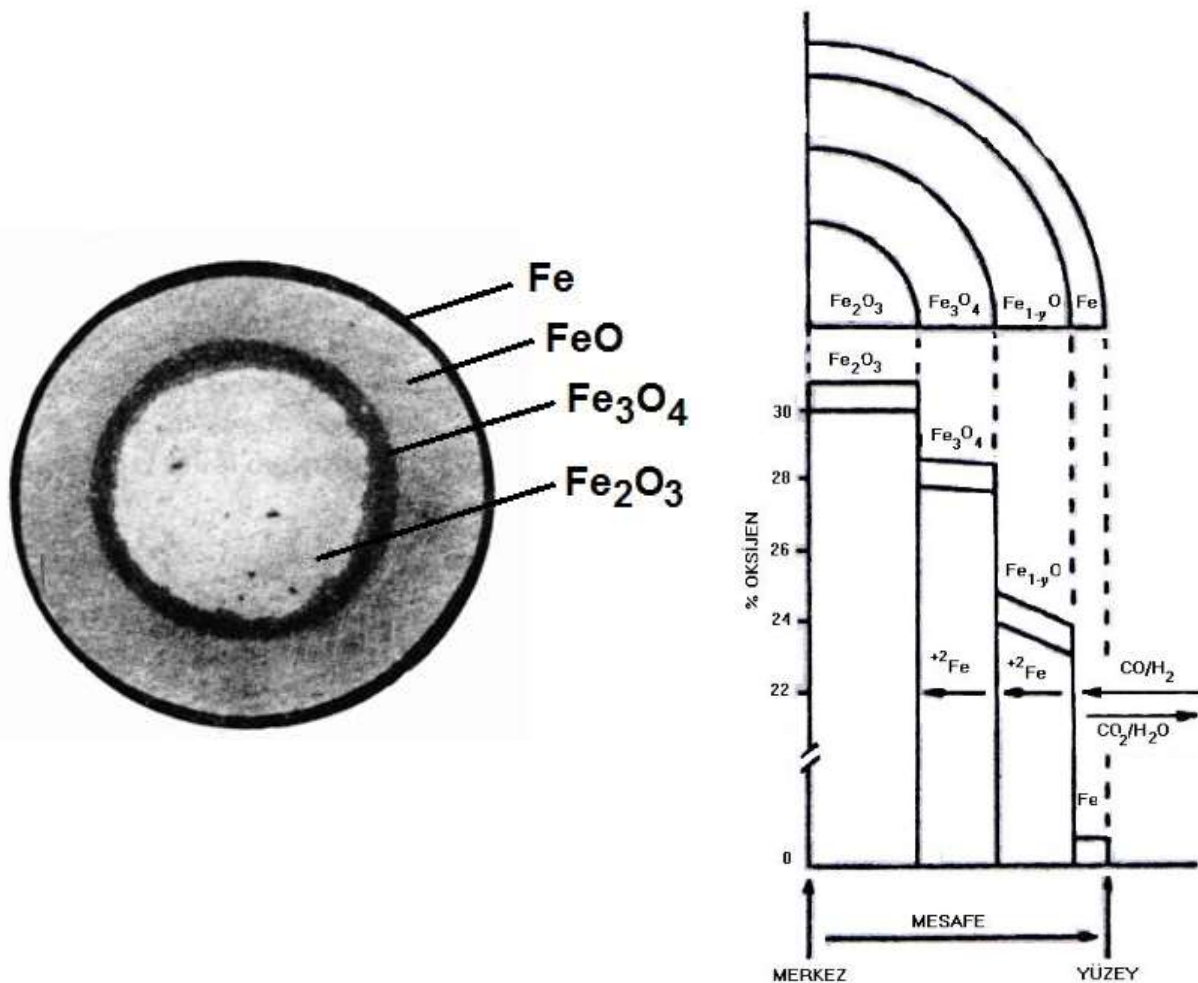


**Figure 4.3** Schematic representation of the reduction of the hematite particle and the topochemicality in reduction [5, 6, 8].

If the reaction products form a layer between the original solids and the gases which react with the gases, such as the oxidation of the metals or the metal sulfides or the reduction of the oxides with gases, the molecules must be diffused from this layer so that the reaction can proceed. Due to the porous or non-porous formation of the reaction product formed by the reactions occurring in the solid state, the kinetics of the reaction will also be different [10-13].

## 4.3. EQUIPMENT AND MATERIALS

1)  Iron ore pellets and coal (coke or lignite dust)

2)  Tube furnace

3)  Precise scale

4)  Graphite crucible

5)  Pens and tongs

## 4.4 EXPERIMENTAL PROCEDURE

1)  In order to observe the reduction behavior, identical pellets are selected from the pellets produced from the obtained from iron concentrate and weighed to determine their weights.

2)  Using the total reduction reaction, the amount of carbon required for the reduction of these pellets and the amount of coal to be used are calculated accordingly. 150% of the theoretical amount of coal calculated on the basis of total pellet weight is weighed and used.

3)  When the tube furnace reaches a temperature of 800 and 1000 ° C, the pellets are buried in the coke bed prepared in the graphite crucible and charged into the furnace with the charging rod.

4)  Pellets are taken from the furnace on the 5th, 10th and 20th minutes respectively, and be cooled to room temperature and weighed after reduction.

The chemical composition of the pellet and coke used in the experiments are given below.

| | $Fe_3O_4$ | $SiO_2$ | $Al_2O_3$ | S | Mn | CaO | MgO | $K_2O$ | $Na_2O$ | P | C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Pellet** | 94,60 | 2,20 | 0,75 | 0,40 | 0,10 | 0,60 | 0,58 | 0,07 | 0,04 | - | - |
| **Coke** | - | 8,26 | 4,30 | 0,54 | - | 1,24 | 0,35 | 0,29 | 0,08 | 0,14 | 80,30 |

Reduction ratios of pellets are calculated using the formula below:

$$\text{Reduction Ratio (\%)} = \frac{\text{Removed Oxygen (wt.)}}{\text{Removable Oxygen (\%)}} \qquad (18)$$

## 4.5 ASSIGNMENTS AND REQUESTS

1)  Write down the aim and procedure of the experiment.

2)  Calculate the required amount of theoretical coal.

3)  Draw the variation of the reduction ratio with time and evaluate the graph.

4)  Calculate the instantaneous reduction rate (dR / dt) at 5th, 10th and 20th minutes.

**5)** For the reduction of ferrous raw materials, under what conditions is the reduction kinetics controlled by chemical reaction, diffusion or mixed controlled? How do you see this difference in the partially reduced iron oxide particle? Schematically draw.

**6)** Using the reactions (4) and (5), plot the % CO - temperature graphs for 700, 800, 900 and 1000 °C temperatures in the total $P_{CO} + P_{CO2} = 1$ atm environment and name the zones. (Bauer-Glaesner diagram plotted against% CO amount).

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**5.1 Objecive:** To investigate the effect of reaction components on cross-linking (hardening, curing) rate of thermoset polymers and to make decorative material from unsaturated polyester resin.

**5.2 Theory:**

Polymers are divided into two groups, thermoplastic and thermoset, in terms of their thermal behavior. Thermoplastics are linear and / or branched chain polymers with no cross-links between their chains. Because of these properties they dissolve in suitable solvents, melt when heated and harden when cooled. These plastics can be heated and cooled many times without significant changes in their properties. They soften and flow under heat and pressure and thus can be shaped in various forms. They are also soluble in suitable solvents and thus can be molded to take various forms. Some of the commonly used thermoplastic polymers are polyethylene (PE), polypropylene (PP), poly (vinyl chloride) (PVC) and polystyrene (PS).

Thermosets are polymers with dense cross-links (networks) between their chains. They are insoluble in any solvents due to their cross-linking, they do not melt when heated, and they degrade when heated to sufficiently high temperatures. Once thermosets are permanently shaped and hardened by a chemical reaction, they cannot be melted by heat or shaped into another form anymore. For this reason, they are molded while in partly polymerized state by heat effect or heat and pressure together. In addition to heat treatment, there are also many polymers that even cure or mature by chemical reactions at room temperature. During molding, the polymerization progresses to plastic cross-linking and the polymer loses its flow property. Because of this, thermosets do not enter into the reproduction process like thermoplastics, meaning they cannot be recycled. Examples of the most commonly used thermoset polymers are phenol-formaldehyde, melamine-formaldehyde, epoxy resins and unsaturated polyesters.

The definition of unsaturated polyester is used for polyester polymers with double bonds (unsaturation) in the polymer chains. Such a polyester resin can be synthesized through a condensation reaction between glycol (an alcohol with two –OH groups) and an equivalent amount of an anhydride (or instead a diacid with two –COOH groups) containing a double carbon-carbon bond (Figure 1). Certain properties in commercial resins can be obtained with different diol and diacid blends. During the condensation reaction, the double bond of the

anhydride does not react and remains on the linear polyester chains. The unsaturated polyester pre-polymer obtained in this stage exhibits thermoplastic properties that can be re-hardened when cooled while being softened and fluidized when heated.
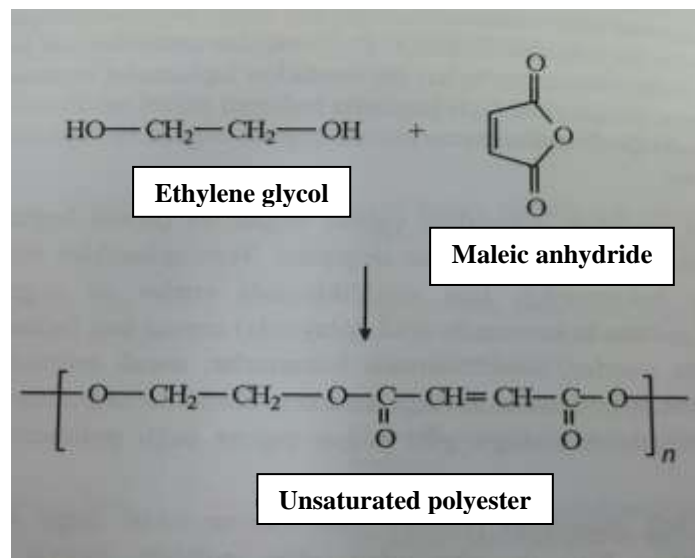


Figure 1: Synthesis of unsaturated polyester.

In the second phase; in the presence of a suitable initiator the unsaturated polyester is heated to the decomposition temperature of the initiator with a vinyl monomer ($CH_2 = CHR$) such as a resolvent styrene, the double bonds in the linear polyester chains are opened and they cross-link (curing, hardening) with styrene molecules via radicalic polymerization mechanism. In the end of this process, the linear and unsaturated polyester chains are copolymerized with a monomer such as styrene into a cross-linked network structure which results in a **thermosetting structure** that does not melt when heated, cannot be reshaped and burns at high temperatures (Figure 2). The quality of this thermosetting structure is closely related to the cross-link density. As the cross-link density increases, the polymer's elastic modulus and thermal stability increase, while the impact strength decreases. The cross-link density is controlled by adjusting the ratio of the input variables (number of unsaturation points) used in the synthesis of the polyester.

In commercial applications, the amount of vinyl monomers varies between 30-50 wt% of monomer-unsaturated polyester mixture. In addition to link unsaturated polyester chains, vinyl

monomers also serve to solve the pre-polymer and affect the properties of the thermosetting structure to be obtained. Styrene is the most widely used monomer because it is a good solvent for unsaturated polyester, it has low viscosity and low prices. The boiling point of the styrene is high so the evaporation loss is low when added to the polyester. However, it is flammable and harmful to health. When the styrene content in the polyester resin is reduced, the volume between the unsaturated polyester chains increases and the stiffness of the thermoset polymer decreases. When more styrene is used, a highly cross-linked polyester is obtained which properties of polystyrene are predominant. Methyl methacrylate, vinyltoluene, diallyl phthalate and $\alpha$-methyl styrene are other monomers used for cross-linking of unsaturated polyester resins.
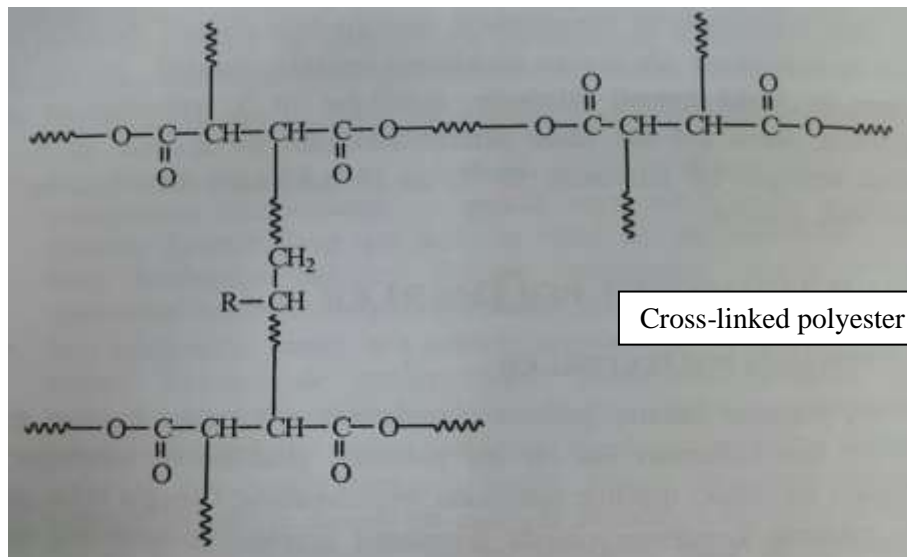


Figure 2: Vinyl monomer-cured cross-linked polyester.

Benzoyl peroxide, cumene hydroperoxide or azobisisobutyronitrile can be used as the initiator. Usually methyl ethyl ketone (MEK) peroxide is used for polyesters that harden at room temperature. The reaction is generally activated with small quantities of cobalt naphthenate. Cobalt naphthenate is an accelerator that increases the decomposition rate of initiator peroxides. Generally, the accelerator is pre-mixed into the resin and by adding the initiator quickly at the last moment, the mixture is poured into the mold. The copolymerization reaction is an exothermic reaction thus, premixing the accelerator with the initiator may cause an explosion. Concentrations of initiator and accelerator directly affect the value of reaction temperature and the duration of curing. Increasing the temperature and the concentrations of initiator and

accelerator shortens the set time but also brings about undesirable results such as air bubbles, surface defects and excessive size reduction with respect to the die. While unsaturated polyesters can be processed in many ways, they are often molded. Pouring into open molds or filling molds by spraying are the methods used for most of the small volume products. Pressure casting is often used in large volume products such as automobile panels.

Unsaturated polyesters have advantages such as easy processing, no volatile byproduct formation, fast crosslinking, light color and dimensional stability. Their physical and electrical properties are good. They are not majorly affected by chemical substances. Resistance to flame, chemicals and aging can be improved by adjusting the composition of the resin mixture. These resins are used in the construction of various parts of electrical and electronic equipment, in the manufacture of goods such as chairs, suitcases, fishing rods, service trays and as matrix materials in composites.

*Glass fiber reinforced unsaturated polyester resins (composite)* are the most widely used reinforced unsaturated polyester resin type. The pre-cured product is a liquid material comprising a mixture of a linear polymer and a liquid monomer. Since this mixture has low viscosity, it is capable of mixing with a high amount of filler material and thoroughly wetting glass fibers. Unsaturated polyesters can be reinforced with up to 80% glass fiber. These reinforced unsaturated polyesters have a strength of 172 to 344 MPa, good impact resistance and chemical resistance when cured (when cross-linking is completed). Glass fiber reinforced unsaturated polyesters are used in the construction of automobile panels and body parts, as well as in the construction of small boat bodies, building panels, bath parts, pipes with high abrasion resistance, water reservoirs and fuel tanks.

### 5.3 Chemical materials and equipment to be used:

Resin:               Unsaturated polyester / styrene mixture

Initiator:            Methyl ethyl ketone (MEK) peroxide

Accelerator:         Cobalt naphthenate

Other materials:      Molds, plastic cups, wooden spatula, mixer, thermometer, chronometer and plastic pipette.

## 5.4 Experimental procedure:

1) Determining gelation time: Prepare 5 plastic cups and number them from 1 to 5. Put 10 grams of resin in each cup. Add 1 wt% cobalt naphthenate in first 3 cups, add 2 and 4 wt% cobalt naphthenate in 4th and 5th cups and mix well. Subsequently, add 0.5%, 1%, 2%, 1%, 1% methyl ethyl ketone (MEK) peroxide in numbered cups respectively and start the timer. Stir for a minute and remove the spatula. Then stir for 10 s after every 60 s. Stop the chronometer when the resin starts sticking to the spatula. Record gelation time for different amounts of initiator and accelerator.

2) Decorative object preparation: Weigh 50 g of resin in a plastic container and add cobalt naphthanate with the amount of 0.5 wt% of resin. Take half of this mixture, add 1 wt% methyl ethyl ketone (MEK) peroxide quickly to the resin, mix rapidly and pour the final mixture into the container. Wait for the reaction to complete. Again add 1 wt% methyl ethyl ketone (MEK) peroxide to the remaining resin and immerse the decorative object to be embedded in the mold in the resin. Wet the object, then place it in the mold and pour resin onto it. Cover it with polyester or acetate paper and remove the final product from the mold after hardening process is complete.

## 5.5 Results and discussion:

1) What is the gelation time you determine in the 1st step of the experiment? Discuss what might be the effects of reaction conditions and environmental factors on gelation time.

2) Draw the changing initiator concentration vs. gelation time you recorded in the 1st step, determine the curve behavior.

3) Draw the changing accelerator concentration vs. gelation time you recorded in the 1st step, determine the curve behavior.

4) Interpret your observations and experimental results on all the stages of the hardening experiment of the unsaturated polyester resin.

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## 6. MECHANICAL TESTS

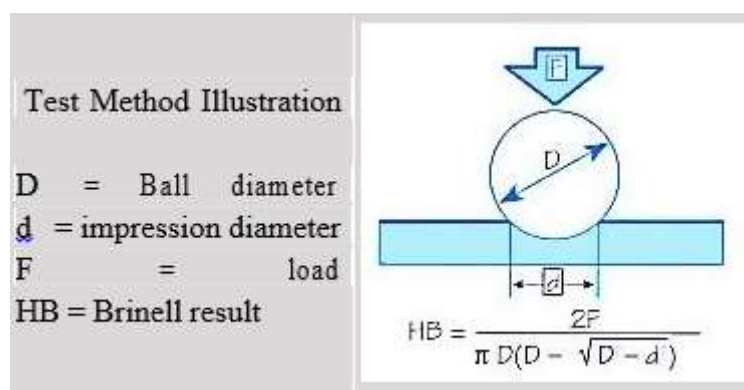## PART 6.1: HARDNESS TESTING

### 6.1.1 AIM

To introduce the principles of indentation hardness testing, emphasizing the limitations and significance of the results.

### 6.1.2 INTRODUCTION

Hardness is generally considered as resistance to penetration. The harder the materials, the greater the resistance to penetration. Hardness is directly related to the mechanical properties of the material. Factors influencing hardness include microstructure, grain size, strain hardening, etc. Generally, as hardness increases so does yield strength and ultimate tensile strength (UTS), thus specifications often require the results of hardness tests rather than tensile tests. The most popular methods are Brinell, Vickers and Rockwell hardness tests for metals and alloys.

### BRINELL TEST

In a standard Brinell test 10 mm diameter hardened steel ball is forced to penetrate the material by 3000 kgf for steels and cast irons. The load and ball diameter selection is important depending on the hardness of materials and 500 kgf is used for softer materials with the same ball diameter. Keeping the ratio of load $P$ to the square of diameter $D^2$ constant (30 for steels and cast irons and 5 for soft metals and alloys), different load and ball diameter combinations can be selected and used in Brinell hardness testing. The Brinell Hardness Number (BHN) is obtained by dividing the applied force P, in kgf; by the curved surface area of the indentation, which is actually a segment of sphere. The geometry of indentation is given in Figure-1, and the hardness is determined according to the relationship,



Test Method Illustration

D = Ball diameter
d = impression diameter
F = load
HB = Brinell result

$$HB = \frac{2F}{\pi D(D - \sqrt{D - d})}$$

where $D$ is the diameter of the indenter ball and $d$ is the average diameter of the indentation, both in mm.
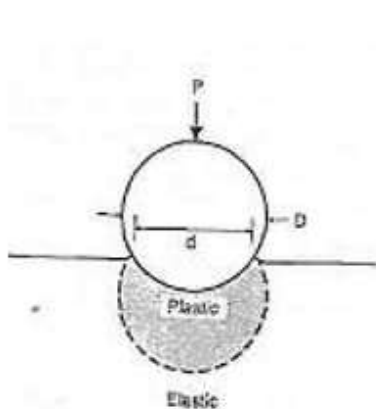
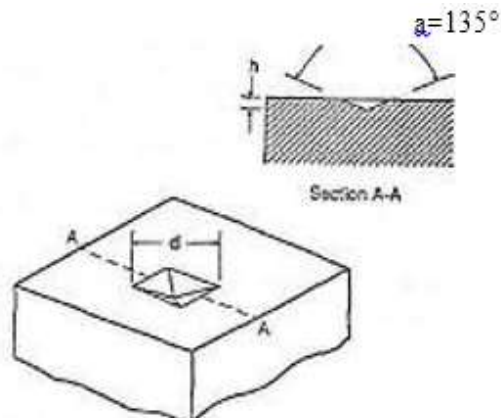Figure-1: Geometry of deformation under a Brinell hardness indenter.

Figure-2: Vickers hardness indentation.

## VICKERS TEST

The Vickers hardness test is based on the same principle as the Brinell test, except the indenter is a diamond pyramid with square base. The angle between the faces of pyramid is $136^0$ as shown in Figure-2. The Vickers Hardness Number (VHN) of materials is obtained by dividing the applied force $P$, in kgf, by the surface of the pyramidal depression yielding the relationship

$$\text{VHN} = \frac{1.8544P}{d_2} \qquad \text{(in some sources VHN is cited as DPH)}$$

where $d$ is the average length of diagonals in mm. Due to the shape and hardness of indenter the method is applicable to metals and alloys with wide variety of hardness. Test load is selected between 1 and 120 kgf depending on the hardness of materials. It is also possible to apply micro hardness testing by keeping the force between 5 grf and 2 kgf in Vickers scale.

## ROCKWELL TEST

In the **Rockwell** test, a diamond cone or a hard steel ball is employed as the indenter depending on the hardness of materials. Diamond cone or *Brale* indenter with cone angle of $120^0$ is used to test hard materials and the balls of sizes between 1.6 mm (1/16") and 12.7 mm (1/2") are used in testing softer materials. Rockwell tests differ from other indentation hardness tests in that the depth of indentation determines the hardness rather than the indentation size (see Figure3). Therefore, surface condition of specimens is very important in Rockwell testing because of its high dependency on the accuracy in indentation depth measurements. In order to establish a reference position a *minor load* of 10 kgf. is first applied, and the major load is then applied. Additional penetration due to *major load* is measured and readings are obtained from a calibrated scale (dial) directly, which has a maximum value of 100, depending on the depth of penetration. Most commonly used Rockwell hardness scales are given in Table-l with typical applications. The hardness numbers are designated *HRX,* where *X* indicates the scale used (i.e.

50 HRC for 50 points on the C scale of dial). It should be noted that a Rockwell hardness number is meaningless unless the scale is not specified.
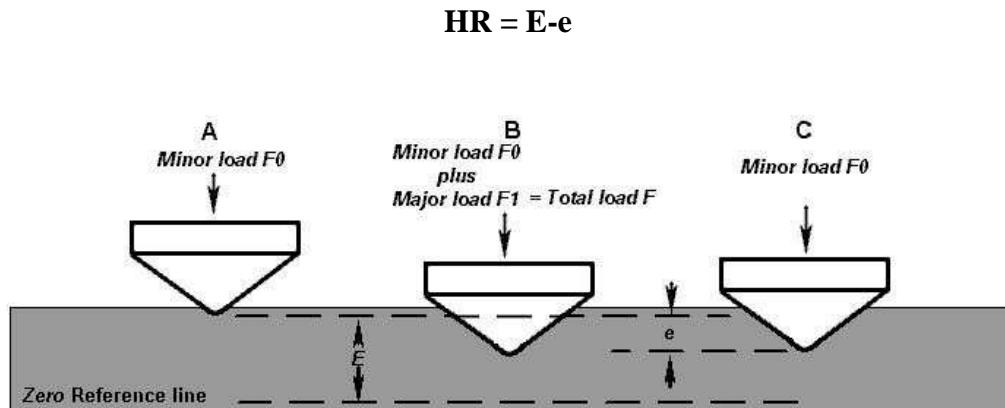
$$HR = E-e$$



Figure 6.3: Increasing depth of penetration in the Rockwell test

Table 6.1: Commonly used Rockwell hardness scales.

| Scale X | Indenter Type | I Major Load (kgf) | Typical Applications |
|---|---|---|---|
| A | Diamond Brale | 60 | Tool Materials |
| D | Diamond Brale | 100 | Cast Irons, Sheet Steels |
| C | Diamond Brale | 150 | Hardened steels and cast irons, Ti alloys |
| B | 1/16" Diameter Ball | 100 | Annealed steels, Cu and Al alloys |
| E | 1/8" Diameter Ball | 100 | Al and Mg alloys, reinforced polymers |
| F | 1/16" Diameter Ball | 60 | Soft sintered products |
| M | 1/4" Diameter Ball | 100 | Very soft metals, polymers |
| R | 1/2" Diameter Ball | 60 | Very soft metals, polymers |

Since the deformations caused by an indenter are of similar magnitude to those occurring at the ultimate tensile strength in a tension test, some empirical relationships have been established between hardness and engineering ultimate tensile strength of metals and alloys. For example, <u>for steels</u> UTS can be **roughly estimated** from Brinell hardness as follows:

UTS (in MPa) = 3.45 x BHN

## 6.1.3 EQUIPMENT

Rockwell hardness tester

Brinell hardness tester

Microhardness (Vickers) tester

Different test specimens

## 6.1.4 PROCEDURE

1.  Determine the proper Rockwell hardness scale,

2.  Calibrate the Rockwell hardness tester,

3.  Take five readings per specimen,

4.  Perform Brinell hardness measurements on designated specimens (3 readings)

5.  Using microhardness tester, determine the VHN at 0.20 mm distances from the surface to the center of case carburized specimen, until the hardness remains unchanged.

6.  Determine the core hardness of the carburized steel

## 6.1.5 ANALYSIS

Calculate the range and mean in hardness values for each test specimen which will be considered in lab report.

## 6.1.6 LAB. REPORT REQUIREMENTS

1.      Results

List hardness values of Rockwell and Brinell for each specimen. List VHN versus distance from surface for carburized specimen.

Determine the effective carburizing depth that corresponds to 400 VHN.

2.      Discussion *(only those indicated will be answered in the lab report)*

2.1.    How do the Rockwell and Brinell tests actually measure hardness? Give any appropriate sketches and formulae. Are there any units involved? Describe the procedure for the Rockwell test, explaining the reason for the pre-load.

2.2.    What is the limitation on the thickness of specimens for a hardness test? Explain. Calculate the minimum thickness for one specimen for the Rockwell test and one for the Brinell test.

3.  What are the limitations for distance from specimen edge to indentation and distance between indentations? Explain why these limitations exist in both cases.

4.  What surface condition is necessary for Brinell, Rockwell and Vickers?

5.  Why is the mean pressure (stress) under the indentor much greater than the yield stress? How much greater is it?

6.   What are the advantages of Vickers test against Brinell test?

## 6.1.7 REFERENCES

Metals Handbook, 9th ed., *Mechanical Testing,* Vol. 8, 1990.

G. Dieter, *Mechanical Metallurgy,* S1 ed., Mc Graw Hill, 1986.

N. Dowling, *Mechanical Behavior of Materials,* Prentice Hall, 1993.

"An Evaluation of the Impression Test for Estimating the Tensile Properties of Metallic Materials, "H.N. Jones, *Journal of Testing and Evaluation,* Vol. 20, pp. 403-407, Nov. 1992.

## PART 6.2: TENSILE TEST AND ANALYSIS OF MECHANICAL PROPERTIES OF A METAL

**6.2.1 SUBJECT:** Tensile testing and evaluation of tensile properties of materials**.**

### 6.2.2 OBJECTIVE:

a)      To become familiar with the principles and capabilities of mechanical testing machines.

b)      To carry out a tensile test on the given metal alloy and polymer specimens.

c)      To understand how to evaluate.

   (i)      Yield strength

   (ii)      Ultimate tensile strength

   (iii)      Fracture stress (normal and actual

   (iv)      Percentage elongation

   (v)      Percent reduction in area

   (vi)      Modulus of Elasticity strength constant ($K$)

   (vii)      Strain hardening coefficient ($n$)

### 6.2.3 PROCEDURE:

The student will observe the testing of the various samples as the mechanical testing machine is operated by the instructor and/or Teaching Assistant.

1.      Measure the specimen dimensions

2.      The specimen is attached the grips of the testing machine (Figure 2).

3.      An extensometer used to measure elongation, is attached to the gage-length of the specimen.

4.      While the specimen is pulled in tension, the data acquisition software collects the load and extension data from the testing machine.

5. The specimen is pulled to failure.

6. The final dimensions of the specimen are measured.

Primary calculations made:

Note down the initial and final dimensions of the sample:

Initial length = $L_0$

Initial width = $W_0$

Initial thickness = $T_0$

Final length = $L_f$

Final width = $W_f$

Final thickness = $T_f$

Initial cross sectional area, $A_0 = W_0 T^*_0$

Initial volume, $V_0 = A_0 * L_0$

**Prep Work**

**Measure the initial diameters and cross-section areas of your specimen.**

**Mark a gauge length.**

Record the direct results from the test.

Elastic Modulus = _____

Ultimate stress = _____

1. Define engineering stress, engineering strain, true stress, and true strain.

2. Check out the cross-sectional area of the test section. Is it your standard ASTM tensile specimen? Check the width and thickness at three different places for the appropriate cross-section dimensions.

3. Discuss the difference between elastic and plastic deformation.

4. Make a copy of the data files from the data acquisition software onto a memory stick.

5.    On your engineering stress strain curves (see 'Results'), discuss and indicate elastic limit, upper yield point, lower yield point, ultimate stress, proportional limit, and fracture stress. Discuss what kind of properties would be observed if the material had a brittle fracture.

6.    Discuss the classical 'cup and cone' fracture (ductile fracture) and type of fracture of cast irons.

7.    List any possible sources of error in your testing and evaluation of engineering stress-strain curve.

**RESULTS:** Use a spreadsheet program (Microsoft Excel, etc.) to calculate and plot true stress-strain curves from the load-extension data collected from the data acquisition software.

Afterwards, calculate:

i.    Modulus of Elasticity, $E$, from the elastic region of stress–strain curves.

ii.   0.2% offset yield strength.

iii.  Fracture strength. (normal and actual)

iv.   % Elongation at Fracture = $\dfrac{L_f - L_o}{L_o} \times 100$

v.    % Reduction of area = $\dfrac{A_o - A_f}{A_o} \times 100$

vi.   Value of the strength constant, $K$, and the strain hardening coefficient, $n$, in the plastic region using:

$$s_T = K \varepsilon^n$$

Actual strain = Elongation / gage length   (gage length = 1 inch)

$$E = \Delta L / L_0$$

Actual Area = $V_i$ / ($L_i$ + Elongation)

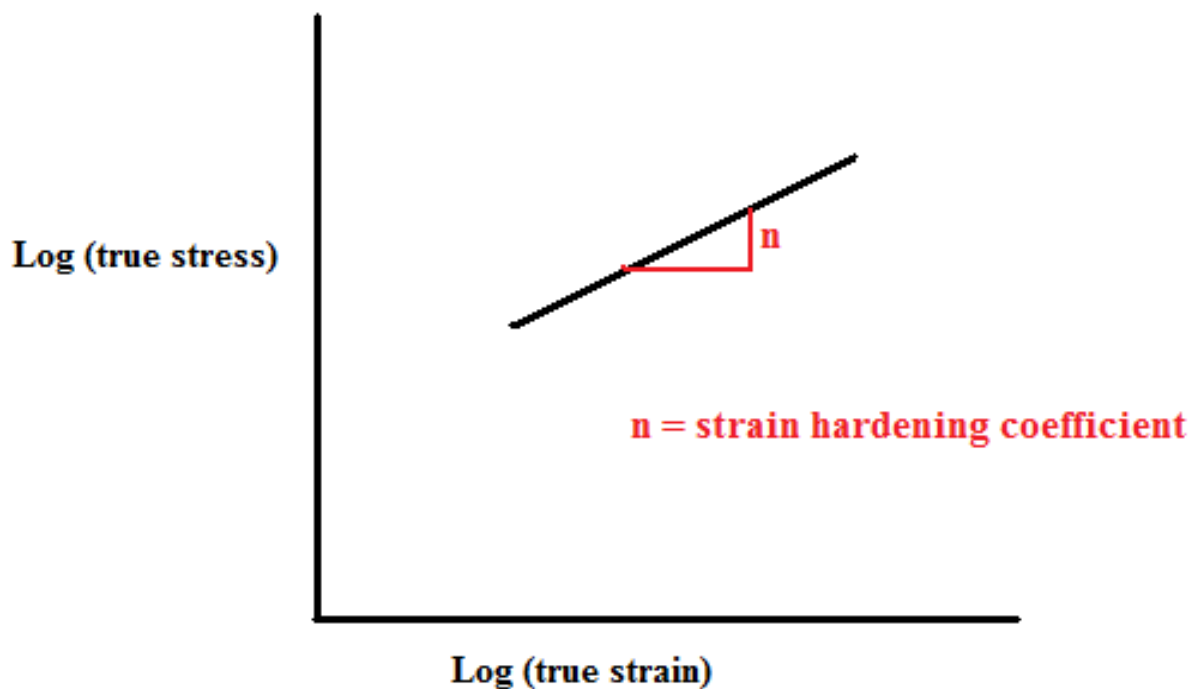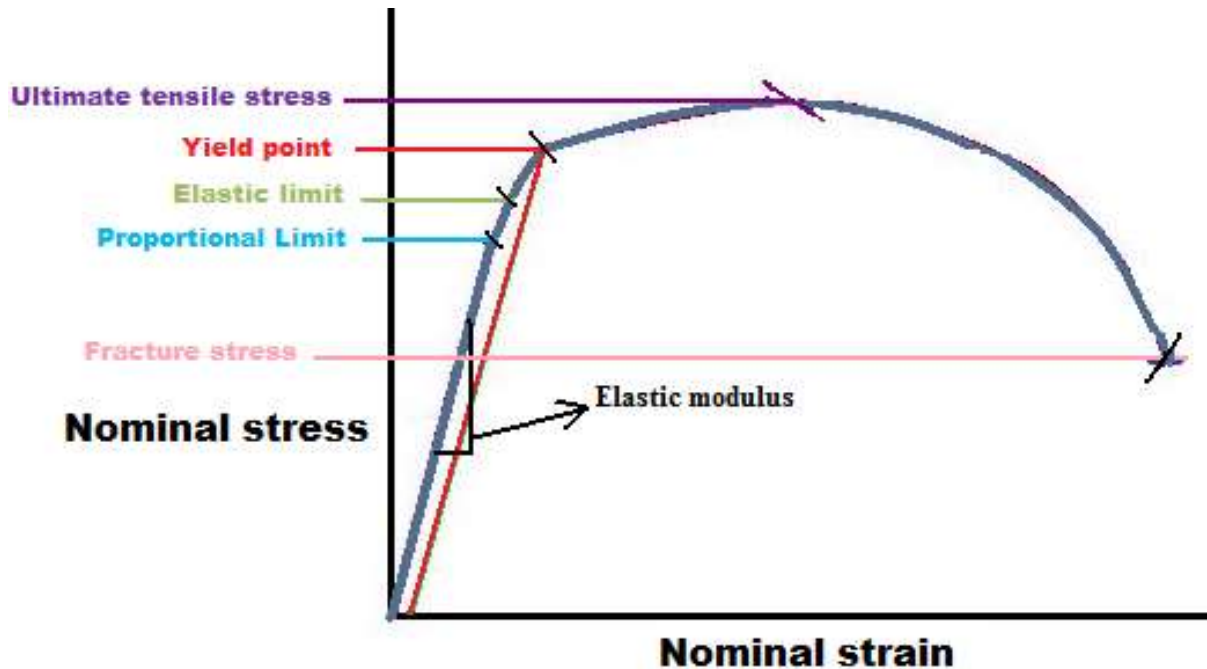Nominal stress = Load / $A_0$

Nominal strain = Elongation / $L_0$

True stress = Load / Actual area = $F/A_0$

4. Draw a graph between Nominal stress (y-axis) and Nominal strain (x-axis); Log (True stress) (y-axis) and Log (True strain) (x-axis), from which the following can be calculated. Sample graphs are shown below:
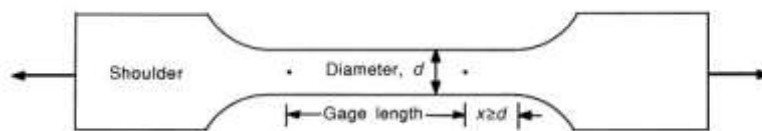




n = strain hardening coefficient

**Note:** Actual stress and true stress are the same; actual strain and true strain are the same.

A picture of Instron® universal testing machine in the Laboratory. More information about the tensile testing machines could be found from the references at the end of the guideline.



Typical tensile specimen
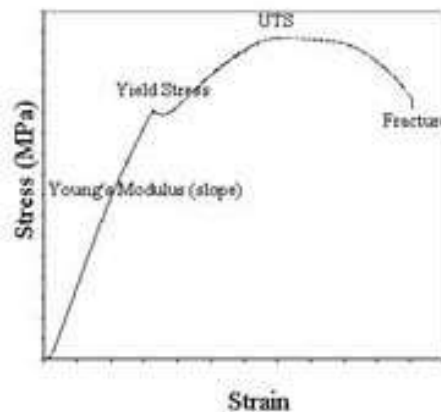


### 6.2.4 REFERENCES:

1.      Annual Book of ASTM Standards, Vol. 03.01, Metals Tests methods and procedures, designation E8, 1995 (or the recent edition) It should be available in the Research Park Reference Library.

2.      ASM Handbook, Mechanical Testing, Vol. 8, ASM-Intl., Materials Park, Ohio (available in the Research Park Reference Library.

## PART 6.3: IMPACT TESTING

### 6.3.1 OBJECTIVE

To conduct Charpy V-notch impact test and determine the ductile-brittle transition temperature of steels.

### 6.3.2 EQUIPMENT

Coolants

Standard Charpy V-Notched Test specimens

Impact tester

### 6.3.3 INTRODUCTION

Notched-bar impact test of metals provides information on failure mode under high velocity loading conditions leading sudden fracture where a sharp stress raiser (notch) is present. The energy absorbed at fracture is generally related to the area under the stress-strain curve which is termed as toughness in some references. Brittle materials have a small area under the stress-strain curve (due to its limited toughness) and as a result, little energy is absorbed during impact failure. As plastic deformation capability of the materials (ductility) increases, the area under the curve also increases and absorbed energy and respectively toughness increase. Similar characteristics can be seen on the fracture surfaces of broken specimens. The fracture surfaces for low energy impact failures, indicating brittle behavior, are relatively smooth and have crystalline appearance in the metals. On the contrary, those for high energy fractures have regions of shear where the fracture surface is inclined about 45° to the tensile stress, and have rougher and more highly deformed appearance, called fibrous fracture.

Although two standardized tests, the Charpy and Izod, were designed and used extensively to measure the impact energy, Charpy v-notched impact tests are more common in practice. The apparatus for performing impact tests is illustrated schematically in Figure-I. The load is applied as an impact blow from a weighted pendulum hammer that is released from a position at a fixed height *h*. The specimen is positioned at the base and with the release of pendulum, which has a knife edge, strikes and fractures the specimen at the notch. The pendulum continues its swing, rising a maximum height *h '* which should be lower than *h* naturally. The energy absorbed at fracture *E* can be obtained by simply calculating the difference in potential energy of the pendulum before and after the test such as,
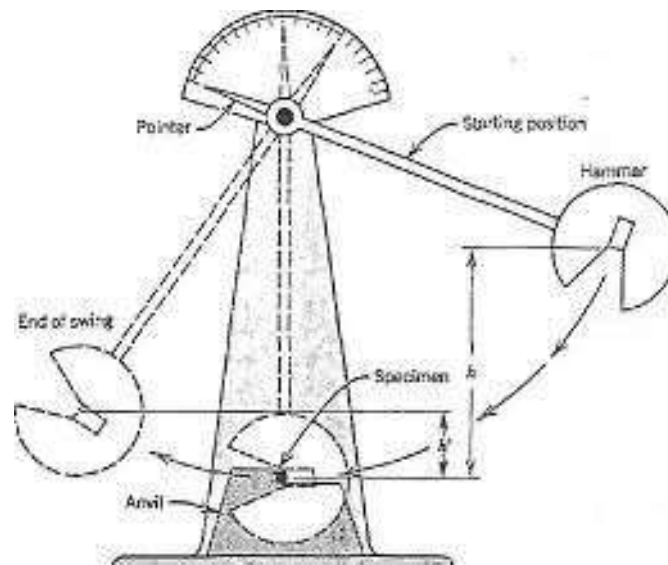
$$E = m.g.(h\text{-}h')$$
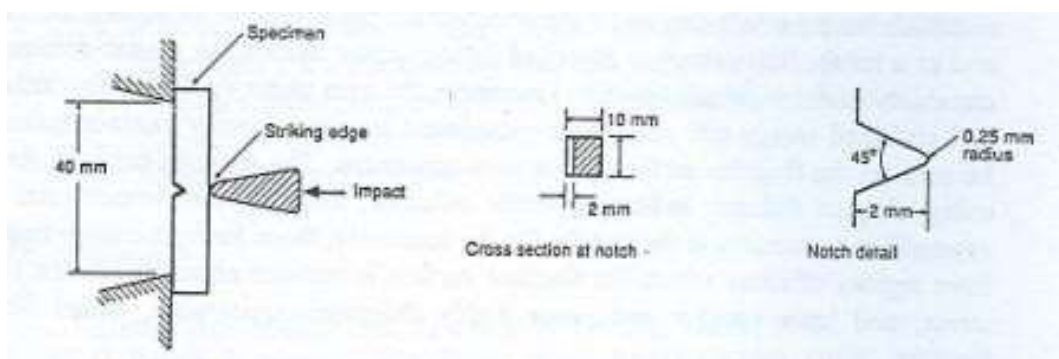
Fig. 1. Apparatus for impact testing of materials.



Fig. 2. Specimen and loading configuration for Charpy V-notched impact test.

Body centered cubic (bcc) metals, particularly steels, often exhibit a decrease in impact energy as the temperature is lowered. The temperature at which a sharp decrease in impact energy occurs is called the ductile-brittle transition temperature (DBTT) as shown in Figure-3 schematically. This transition temperature is generally chosen as a lower limit for the application of such metals.

Some steels may show transition characteristics in their failure mode from ductile to brittle gradually as temperature is decreased, which is given in Figure-4 schematically. In this case, different approaches may be used in determining transition temperature but the average energy concept is the most popular one. Determination of transition temperature can also be done by examining the fracture surfaces of specimens tested at different temperatures. For example, the temperature, at which the fracture surface consists 50 percent cleavage (crystalline) and 50 percent ductile (fibrous) types of fracture, is called fracture appearance transition temperature (FATT). Another common criterion is to determine the transition temperature on the basis of

an arbitrary energy absorbed. For example, *20 J transition temperature* is an accepted criterion for low-strength ship steels.
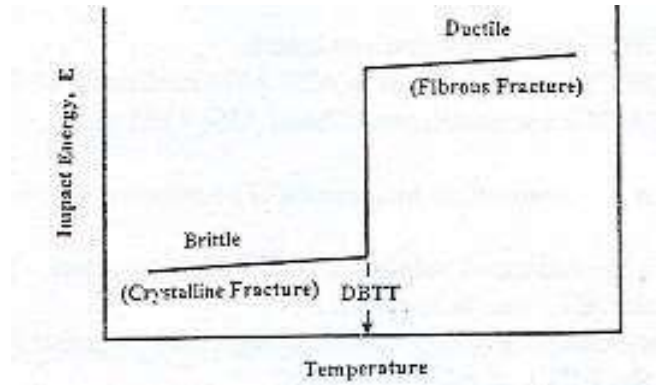


Fig. 3. Typical ductile-brittle transition curve for annealed low carbon steel.
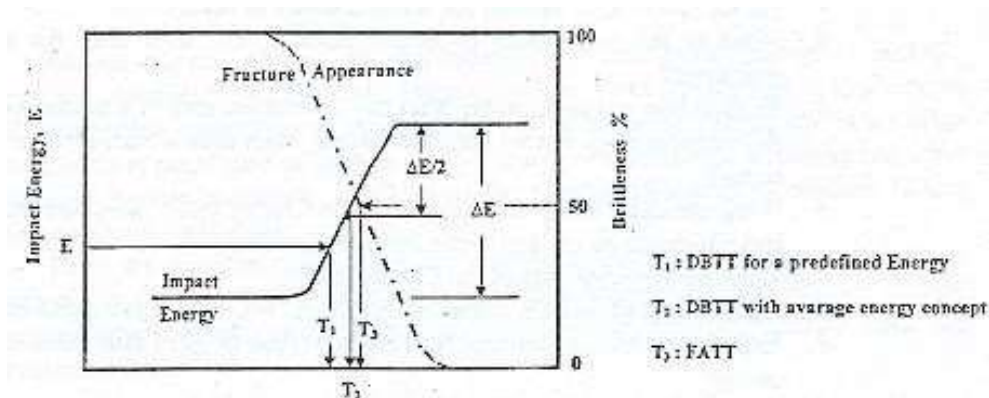


Figure-4: Various criteria of transition temperature obtained from Charpy tests.

### 6.3.4 PROCEDURE

Note: Test one material with two specimens for each temperature,

**1.** Check the zero calibration of the impact tester.

2. First, test a specimen at room temperature.

3. Based on the room temperature result, decide whether to concentrate on higher or lower temperature.

4. Test specimens over a selected range of temperatures, attempting to establish fully ductile test, a fully (or nearly) brittle test, and as many temperatures in between as possible.

5. Note fracture energy and estimate the % brittleness from the appearances of fracture surfaces of the specimens.

## 6.3.5 LAB REPORT REQUIREMENTS

1.  Results

    Display the test data in a Table.

    Plot impact energy versus temperature and % brittleness versus temperature.

    Find DBTT of the steel that you tested.

2.  Discussion *(the questions will be answered in the lab report)*

Give the estimated values of DBTT for your steel. Suggest 2 ways in which DBBT can be lowered.

What are the 3 basic factors which contribute to brittle fracture of steels? Do all 3 have to be present for brittle fracture to occur?

Explain how a triaxial stress state can arise at the root of a notch. Would this occur in thick or thin material? Thus, when does a biaxial stress state occur.

What are the main uses of the Charpy test?

List the ASTM and TS specifications for the two impact tests with titles.

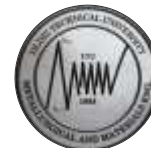Explain the relation between fracture toughness ($K_{IC}$) of steels and impact energy.

Explain the effect of carbon content on transition behavior of plain carbon steels in annealed condition.

Explain the effect of manganese on DBTT of steels.

**REFERENCES**

> **1.** Metals Handbook, 9th ed., *Mechanical Testing,* Vol. 8, 1990.
>
> **2.** G. Dieter, *Mechanical Metallurgy,* SI ed., Mc Graw Hill, 1986.
>
> **3.** N. Dowling, *Mechanical Behavior of Materials,* Prentice Hall, 1993.
>
> **4.** ASTM and TS Standards.

ASM Metals Handbook, 9th ed. Vol. 12.

## 7. LEACH AND CEMENTATION

### 7.1 OBJECTIVE OF THE EXPERIMENT

Investigation of copper solubility and parameters affect this solubility in acidic solutions of copper sulphate and chalcopyrite based copper ores. Precipitation of copper in the solution by using cementation process and determination of parameters which affect the efficiency.

### 7.2 THEORETICAL INFORMATION

**Solutioning Process (Leaching)**

Generally hydrometallurgical processes are carried out in two stages. First stage is the leaching process and in this stage is selectively solutioning of metals by interaction of ore minerals with an appropriate solvent. Second stage is regaining of metals from solutions.

Leaching is a wide spread process it includes sectors from mining to metal production. The solvent in the leach process can be water, acid, alkaline, salt based or combination of them. An the dissolving material can be ore, concentrated ore, free metal, compounds like sulphur, carbonate, silicate and sulphate or flue dust, intermediate product and any waste includes metal.
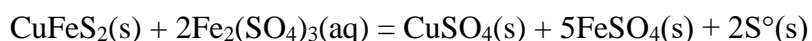
Ores can be subject to some preparation treatments between furnace productions and leach process. Pretreatments before the leaching are crushing, grinding, beneficiation and roasting.

Purpose of the leach process is increase selective dissolution efficiency, rapid dissolution efficiency and total dissolution efficiency. Beneficial minerals should be selectively dissolved in leach process. Because with selective leach, reactant consumption is minimized and clean solutions are obtained for metal regaining sequence. Solvent composition and concentration, dissolution temperature, time and solid in pulp ratios are main variables of the leach process that need to be controlled.

Copper ores usually are processed by pyrometallurgical routes for a long time. However pyrometallurgical techniques are recently replaced with hydrometallurgical ones. Sulphur dioxide ($SO_2$) emission, requirement of ore beneficiation, loss of other metals and high costs are disadvantages of pyrometallurgical techniques. In hydrometallurgical processes, main principal is dissolving of valuable elements by using selective reactants.

In hydrometallurgical technique, copper ore is dissolved with an appropriate leach solution after crushing and grinding processes. Then metallic copper is produced from this solution. Sulphuric acid, ammonia, ammonium salts, chloride-sulphate solutions, nitrate solutions and solutions include microorganisms can be used for leaching process of copper ores.

Chalcopyrite is the most common copper ore so hydrometallurgical researches and efforts are focused on this kind ores. Reactions of chalcopyrite mineral in the sulphuric acid leach solution are given below.

$CuFeS_2(s) + 2H_2SO_4(aq) = CuSO_4(aq) + FeSO_4(aq) + 2H_2S$

$CuFeS_2(s) + 2Fe_2(SO_4)_3(aq) = CuSO_4(s) + 5FeSO_4(s) + 2S°(s)$

Roasting process before leaching can have some economic and environmental problems like pyrometallurgical techniques. These kinds of problems can be eliminated by direct leaching of sulphur based ores that grinded into right dimensions. Direct leach is easily applied to oxide based ores. However for sulphur based ores in atmospheric conditions highly oxidant environments ore in autoclaves high temperature and high oxygen pressure are needed.

**Dissolution Mechanisms**

Reaction rate in leaching; shows how the reaction product or reactant concentrations changes over time in the reaction. As it is known, the dissolution rate in leaching generally decreases with time. This situation; as the reaction time progresses, the surface area of the reaction becomes smaller due to the reduction of the solvent concentration or the formation of a protective layer on the surface (passivation). The dissolution rate is also directly dependent on the activation energy. The magnitude of the activation energy in leaching processes indicates the difficulty of dissolution. In other words, hardly soluble minerals have high activation energy.

**Factors Affecting Leaching**

Most hydrometallurgical processes involve heterogeneous reactions (the type of reaction between multiple phases). The rate of these reactions depends primarily on the hydrodynamics of the leaching system (such as mixing and diffusion) and the chemical interactions of the components present in the system. Clearly, leaching of any ore in an aqueous environment is influenced by the following factors:

1. Grain size of the ore, 2. Composition of the ore, 3. Composition and concentration of the solvent, 4. Contact time of the ore with the solvent, 5. Leaching temperature
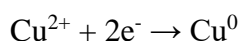
**Cementation**

Any metal in the solution dissolves another metal (granule, plate, powder, scrap) that has a more negative electrode potential than it in the EMF series of metals is called "cementation". The cementation process is applied either to the production of a metal or to the removal of impurities from the electrolyte. When copper production is taken as an example, cementation becomes a matter of evaluation of poor solutions.
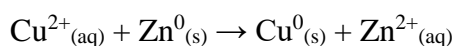
Reactions occurring in copper cementation process:

1. Formation of $Zn^{2+}$ ions by anodic half-cell reaction:

$Zn^0 \rightarrow Zn^{2+} + 2e^-$

2. Formation of metallic copper by cathodic half-cell reaction:

$Cu^{2+} + 2e^- \rightarrow Cu^0$

3. Total cell reaction:

$Cu^{2+}_{(aq)} + Zn^0_{(s)} \rightarrow Cu^0_{(s)} + Zn^{2+}_{(aq)}$

The pH value of the solution applied to the cementation is extremely important. Hydrogen ion concentration in acidic media is high:

$2H^+ + 2e^- \rightarrow H_2$ the secondary reaction evolving according to the reaction is activated. Thus, there is unnecessary increase of cementator consumption. When cementation is being done, the solutions are either not mixed or very slowly mixed that not allowed to aeration. In case of excessive oxygen dissolves in the solution because of severe mixing metallic Zn and Cu move into ionic state as a result of oxygen reduction.

Anodic reaction:

$Zn^0 \rightarrow Zn^{+2} + 2e^-$

Cathodic reaction:

$Cu^0 \rightarrow Cu^{+2} + 2e^-$

$1/2\ O_2 + 2H^+ + 2e^- \rightarrow H_2O$
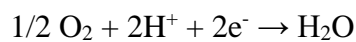
**Cementation Chemistry:** If an iron component is immersed in an aqueous solution containing copper ions metallic copper tends to precipitate, while iron tends to go through the solution. Electrochemical potential is the driving force of this reaction. This potential is calculated with Nernst equation given in (2) below.

$Fe^0 + Cu^{2+} = Cu^0 + Fe^{2+}$ (1)

$E = E^0 + (RT\ /\ nF)\ x\ \ln(a_{Me})$ (2)

In this equation,

E = Real potential (V)

$E^0$ = Standard potential (V)

R = Gas constant

T = Temperature (K)

n = Oxidation level

F = Faraday constant $(C.mol^{-1})$

a = Activity

If the Nernst equation would apply to the copper iron couple;

$E_{Cu} = E_{Fe}$ (3)

$E^o_{Cu} + (RT/nF)\ x\ \ln\ (a\ _{Cu}^{2+}) = E^o_{Fe} + (RT/nF)\ x\ \ln\ (a\ _{Fe}^{2+})$ (4)

$0.34 + (0.059/2)\ x\ \log\ (C\ _{Cu}^{2+}) = -0.444 + (0.059/2)\ \log\ (C\ _{Fe}^{2+})$ (5)

$\log\ (C\ _{Fe}^{2+}\ /\ C\ _{Cu}^{2+} = 26.57$ (6)

$(C\ _{Fe}^{2+}\ /\ C\ _{Cu}^{2+}) = 10^{27}$ (7)

This result theoretically means that there is only 1 copper ion $(Cu^{2+})$ per $10^{27}$ iron ions $(Fe^{2+})$ in solution after cementation. This very large ratio means that the reaction (1) completely moves to right side. According to reaction (1) 1 molar iron (55.85 g) cementite 1 molar copper (63.54

g). This value is determined as 1 kg iron per 1 kg of copper. In industrial applications 1.5-2.5 kg iron is required due to the following side reactions.

$$Fe^0 + 2Fe^{3+} = 3Fe^{2+} \tag{8}$$

$$Fe^0 + 2H^+ = Fe^{2+} + H_2O \tag{9}$$

The oxygen of the air is directly oxidized +2 valence iron causing iron consumption.

The selection of metals in the cementation process is made according to the EMF series.

EMF Series

| Reaction | $E^0, V(SHE)$ | |
|---|---|---|
| $Au^{3+} + 3e = Au$ | +1.42 | Noble |
| $Pt^{2+} + 2e = Pt$ | +1.2 | ↑ |
| $O_2 + 4H^+ + 4e = 2H_2O$ | +1.23 | |
| $Pd^{2+} + 2e = Pd$ | +0.83 | |
| $Ag^+ + e = Ag$ | +0.799 | |
| $O_2 + 2H_2O + 4e = 4OH^-$ | +0.401 | |
| $Cu^{2+} + 2e = Cu$ | +0.34 | |
| $Sn^{4+} + 2e = Sn^{2+}$ | +0.154 | |
| $2H^+ + 2e = H_2$ | 0.00 | Reference |
| $Pb^{2+} + 2e = Pb$ | -0.126 | |
| $Sn^{2+} + 2e = Sn$ | -0.140 | ↓ |
| $Ni^{2+} + 2e = Ni$ | -0.23 | |
| $Co^{2+} + 2e = Co$ | -0.27 | |
| $Cd^{2+} + 2e = Cd$ | -0.402 | |
| $Fe^{2+} + 2e = Fe$ | -0.44 | |
| $Cr^{3+} + 3e = Cr$ | -0.71 | |
| $Zn^{2+} + 2e = Zn$ | -0.763 | |
| $Al^{3+} + 3e = Al$ | -1.66 | |
| $Mg^{2+} + 2e = Mg$ | -2.38 | |
| $Na^+ + e = Na$ | -2.71 | |
| $K^+ + e = K$ | -2.92 | Active |

## 7.3 EQUIPMENT AND MATERIALS

1. Chalcopyrite ore

2. Copper sulphate

3. Sulphuric acid

4. Purified water

5. Precise scale

6. Heated Magnetic Mixer

7. Mixed water bath

8. Pipette, washing bottle, beaker, funnel, filter paper

| **Element (wt %)** | | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Cu** | **Fe** | **Co** | **Zn** | **Ni** | **Au (ppm)** | **Ag (ppm)** |
| Küre ore | 1.5-2 | 47-49 | 0.08-0.12 | 0.1-0.5 | 0.3-0.4 | 0-0,5 | - |
| Küre) concentrated ore | 18-20 | 47-49 | 0.08-0.12 | 0.1-0.5 | 0.3-0.4 | 4-4.5 | 20-22 |

## 7.4 EXPERIMENTAL PROCEDURE

1. The chalcopyrite concentrate which have been prepared for leaching after size reduction and drying are dissolved in sulfuric acid at 50 °C with 1/50 solid liquid ratio.
2. The amount of dissolved in solution is analyzed by Atomic Absorption Spectrometer.
3. The reason for the high or low dissolution efficiency value is discussed.
4. Prepare a $CuSO_4$ solution containing 5 g/200 ml. Cementation is carried out using Fe and Zn metal powders at different pH values (pH = 3, pH = 5 ) in order to observe the cementation process and to determine optimum metal precipitation conditions. The precipitate is separated from the solution by filtration.
5. Copper recovery rate is calculated for each test group.
6. All the results obtained are interpreted.

**Calculations**

**Calculations for Leaching Process:**

Leaching efficiency % = [Amount of Cu passing through the solution (mg / l) / Amount of Cu in the sample (mg / l)] x100

**Calculation of Cementation Process:**

% Cementation efficiency % = [amount of precipitated copper (g / l) / amount of copper in solution (g / l)] x 100.

## 7.5 ASSIGNMENTS AND REQUESTS

2. Calculate precipitated copper efficiency using the results of Cu analysis after precipitation and filtration of the precipitated parts obtained in the test results with $CuSO_4$ solution containing 5 g / 200 ml Cu with Fe and Zn powder.
3. Explain the relationship between precipitation efficiencies and pH values.
4. Which sementator provided higher efficiency? (Zn or Fe) Explain in detail.
5. Calculate the leaching efficiency of chalcopyrite concentrate. Is the efficiency value high or low? What is the reason of this situation?

HOMEWORK: Explain the working principle of the Atomic Absorption Spectrometer.

## 7.6 REFERENCES

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## 8. RECYCLING

### 8.1. OBJECTIVE OF THE EXPERIMENT

The objective of this experiment is to inform the students about secondary aluminum production processes from the scrap.

### 8.2. THEORETICAL INFORMATION

### FUNDAMENTAL DEFINITIONS

**Waste:** Materials and items that need to be disposed or already disposed.

**Reuse:** Repeatedly using of wastes until they reach the end of their economic lifetime, without any treatment other than collecting and cleaning.

**Recycling:** Operation of bringing materials back to manufacturing processes as a raw material after their lifetime has ended.

**Recovery:** Physical, chemical or biochemical methods to transform the components of the waste into other products or different forms of energy depending on the characteristics of the waste. Definition of recovery also includes both reuse and recycling phenomena.

**Recycling Rate:** Ratio of the total amount waste recycled to the total amount of waste generated.

The main scraps used for the aluminum recycling are;

- Beverage cans,
- Aluminum foil wastes, cake pans, and some other kitchenware,
- Plates,
- Window profiles made of aluminum,
- Outdoor and patio furniture,
- Cables,
- Aviation scraps,
- Automotive scraps,
- Extrusion, casting and machining processes sourced scraps.



**Figure 8.1** Images of some aluminum scraps

At the first step, soiled and used aluminum pieces which may be painted or coated are delivered to the conveyor with other packaging wastes. Throughout the conveyor, waste pile is passed through some large magnets in order to remove iron-based and some other metals. Separated aluminum wastes are crushed and baled via scrap baling machine thereafter to be delivered to production facility. Main reason of baling is minimizing the logistic expenses. Baled aluminum may contain excessive moisture which may cause burst in furnace at high temperatures. In order to prevent this incident bales are crushed first. Afterward, crushed pieces are placed into hot furnace for removal of present paint, moisture and other pollutions at working temperature. After removal stage, aluminum is molten for forming processes at 720 °C in a rotary furnace with accompanying stirring to attain complete melting. Prosess gases need to be removed with powerful fans then to be cooled and treated in industrial filter bags for removal of residual particles before releasing to atmosphere through high chimneys. Molten aluminum accumulated at the bottom of the furnace is collected to cast into desired moulds. After several steps they can be used for diverse applications again.
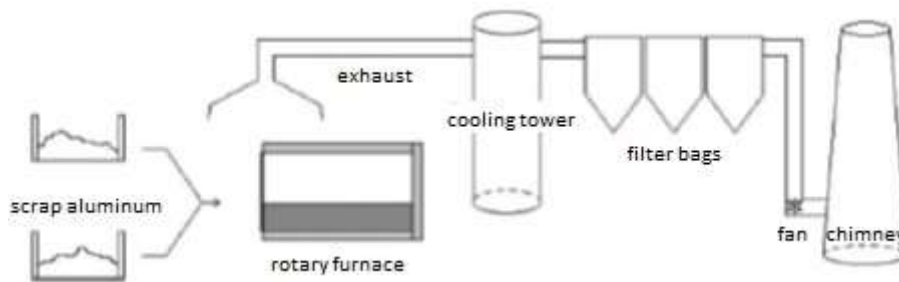


**Figure 8.2** Image of aluminum recycling unit

Recycling of used aluminum not only creates more space for wastes, it also reduces the consumption of bauxite ore and energy.

When one ton of aluminum is produced from used aluminum;

- 1.300 kg bauxite,
- 15.000 liter cooling water,
- and 860 liter prosess water are consumed less.
- 2.000 kg $CO_2$ and 11 kg $SO_2$ are less emitted.

Required energy for producing aluminum from scrap is less almost twenty times than required for producing from bauxite ore. Also it reduces the emission of pollutant gases by %99, greenhouse gas emission by %95 and waste water pollution by %97 rate so recycling contributes energy-saving furthermore it is environment friendly.

## IRON AND STEEL RECYCLING

Iron is third most abundant metal in the Earth's crust. The metal iron can be obtained from iron ores and it rarely exists as the element iron. Haematite, limonite, goethite, magnetite, siderite and pyrite can be listed as the well-known iron ores. To obtain metallic iron, the impurities in the ore must be removed by chemical reduction and it is mainly used in steel making which can be regarded as a carbon alloy. When iron is heated with carbon to a temperature of 1150-1200 ° C, the resulting melt is an alloy containing 96.5% Fe - 3.5% C

and called cast iron or pig iron. This product can be cast in fine details, although it remains extremely fragile to be formed as long as it is not decarburized to remove the most of contained carbon.

Classification of steel scraps by source:

- Circulating scrap; scraps that are acquired from units like steelworks, foundry and rolling plants with well-known chemical analysis and high quality.
- Old Scrap; especially automobile bodies sourced scraps which containing slight amount of phosphorus and sulfur.

For iron and steel recycling, foreign substances in the scrap which have lower oxygen affinity than iron like copper and tin should be taken care of during the process.



**Figure 8.3.** Images of iron and steel scraps

Recycling in iron and steel industr is mainly carried out in electric arc furnaces which is a good option for iron and steel making. Unlike the basic oxygen steelmaking method, cold metal (scrap) is used in electric arc furnaces instead of hot metal. The scrap steel is poured into an electric arc furnace with a crane from the top and furnace is closed with a cover subsequently. This cover carries three electrodes those dip into the furnace. The electricity passing through the electrodes creates an arc, and the heat that comes out melts the scrap. The amount of electricity used in this process is high enough to meet the energy needs of a city with 100,000 people. Other metal alloys can be added to obtain the required chemical composition in the smelting process. The oxygen is also blown to purify the desired steel iron.



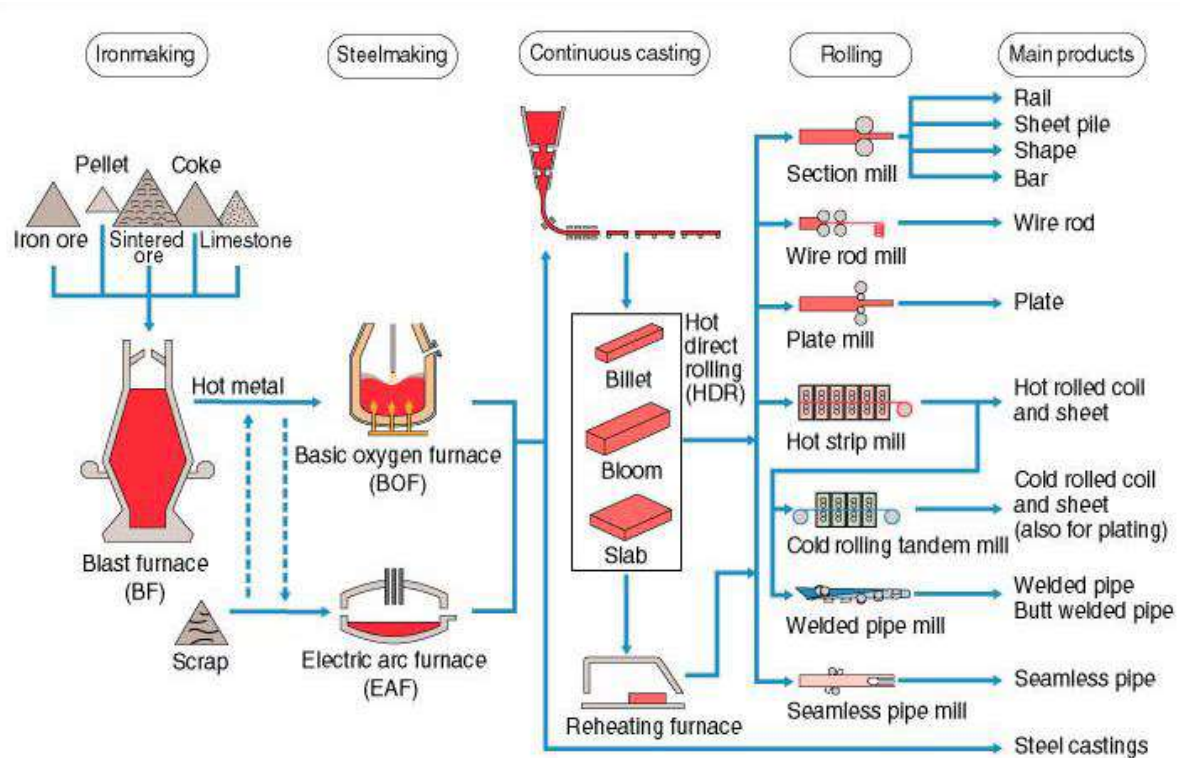**Figure 8.4** Image of operating electric arc furnace

**Figure 8.5** General flow scheme of iron and steel making

## RECYCLING OF COPPER

Following scraps are generally used for secondary copper production;

- Wire rods
- Heat exchangers
- Copper tubes
- Cables and electrical connectors
- Electromotors, generators, transformer coils
- Miscellaneous copper plates and sheets.



**Figure 8.6** Images of copper scraps

Copper production from scrap is usually made in two ways;

1. Melting at a copper smelter along with copper ore
2. Melting along with a proportion of copper ingots at a dedicated copper recycling plant

At a copper smelter, the scrap copper and alloy components are loaded into the furnace which is then fired up. The copper ore is fed into the furnace along with the required amount of limestone and sand. Oxygen and air are supplied and when the mix has become molten, it is then tapped into rectangular molds. The resultant rectangular plates are then purified to 99.9% pure copper using electrolysis processing.

At a copper recycling plant, the bales of compacted copper along with the required content of alloys are loaded into a furnace along with a proportion of pure copper ingots.

The furnace can either be of an electric induction type or a reverberatory one. The electric furnace melts all the contents and tips to pour the molten copper through a spout into molds for either further processing or they are shipped to a copper smelter.

A reverberatory furnace is a square box structure lined with firebricks and is usually gas fired, having a loading door at the front which can be lowered or raised as required. Once the copper is molten, samples are taken, and when approved, the molten copper is poured into molds and left to cool. The resultant copper ingots can be sent for further refining or dispatched to a copper smelter for further processing.

- The cost of copper from scrap is lower than from ore. The recycling of 1 ton of copper from the waste/scrap saves 85% of the total energy consuming comparing to primary production.
- Considering that 12-13% of the reserves are used in the world, it seems that their life span is limited, via recycling the existence of raw material resources is extended.
- The storage and removal of municipal solid waste are highly expensive processes. With recycling operations this expenses can be lowered and those waste product can be reused as raw materials.
- Recycling is more environment friendly process due to less gas and dust releasing during the whole steps.

## 8.3 EQUIPMENT AND MATERIALS

**Materials**

- Aluminum scrap
  - Thick scrap (Excessive parts of cast products)
  - Fine scrap (Chips from machining process)
- Flux (composition will be given during the experiment.)

**Devices/Equipment**

- Melting crucible
- Melting furnace
- hydraulic press
- Cylindrical steel mould

- Oven
- Precision scale
- Mould for casting

## 8.4 EXPERIMENTAL PROCEDURE

On the first step, thick scrap at the half of the total charge is weighed and placed in the furnace with melting crucible at 730 °C for melting. Liquid metal forms in the crucible at the end of this process. During the melting of thick scrap, fine scrap chips are briquetted using a hydraulic press in a cylindrical steel mold. At this step, compressive pressure of the press and fill factor of the briquettes will be measured. Before being placed in the melting crucible, briquettes are preheated for some time. Preheating time and temperature will be determined during the experiment. Subsequently, the briquettes are added to the liquid metal pool in the crucible. During the melting process of the briquettes, the powdered chemicals that will form the flux are weighed on a precision scale and mixed in a container. The mixture is added into the crucible and mixed in liquid metal with a metal rod. After standing in a furnace for about ten minutes, liquid aluminum is cast into a metal mould and solidified. On the last step cast metal will be weighed to calculate total melt and recycling efficiency.

## 8.5 ASSIGNMETNS AND REQUESTS

Whole necessary calculations will be made by students and further assignments will be given during the experiment.

## 8.6 REFERENCES

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## 9. REDUCTION ELECTROLYSIS

### 9.1 OBJECTIVE OF THE EXPERIMENT

The objectives of present experiment are to get information about kinds of electrometallurgy, carry out the electrolysis of copper sulphate solution and to link their findings with the industrial electrolytic refining of copper. The results of this experiment can lead to a discussion about electroplating and the electrolytic refining of copper.

### 9.2 THEORETICAL INFORMATION

### 9.2.1 WHAT IS ELECTROMETALLURGY?

Electrometallurgy is the recovery and purification of metals through electrolytic processes by using electrical energy.

Electrometallurgy makes use of electrothermal and electrochemical processes. Electrothermal processes are used toextract metals from ores and concentrates and to produce and refine ferrous and nonferrous metals and alloys based on themetals extracted. In such processes, electric energy is used as a source of heat.

Electrometallurgy deals with technical aspect of metal electrodeposition. The electrometallurgical processes can be categorized into four main groups: Electrowinning, Electrorefining, Electroplating, Electroforming. The schematic representation of electrometallurgical processes is shown in Fig. 1
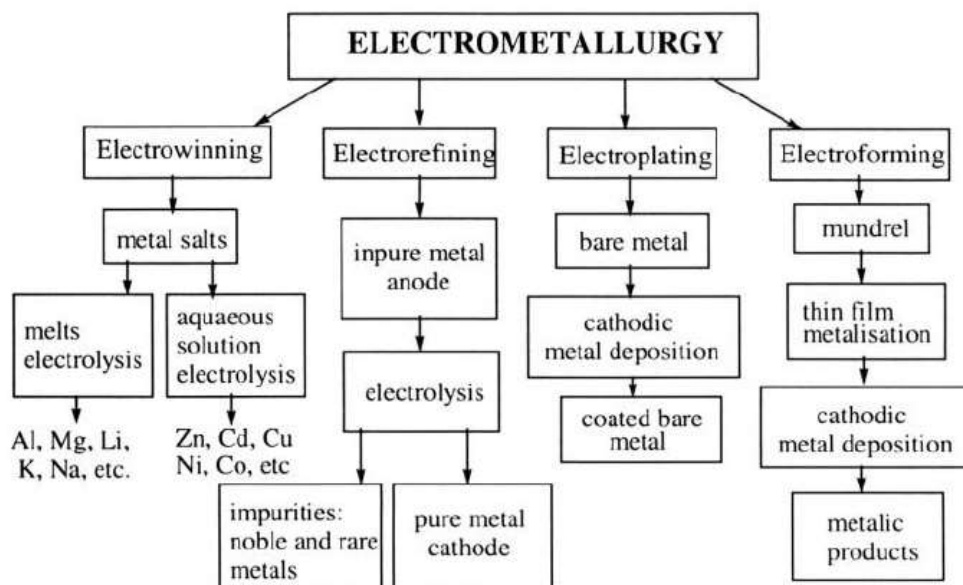


**Figure 1**. Schematic illustration of electrometallurgical processes.

*Electrowinning* is the extraction of metals by electrodeposition from aqueous solution or melts of their salts. On a large scale electrodeposition from molten salts is used for extraction of electronegative elements which cannot be electrodeposited from aqueous solutions, such as aluminum and magnesium, as well as very pure copper, zinc and cadmium by electrodeposition from an aqueous solutions of the metal salts1.

*Electrorefining* is the purification of metals by electrolysis. The impure metal is dissolved anodically and pure metal is deposited catodically, while the impurities being left as anode sludge or as ions in the solution. Many metals are electrorefined such as copper because of conducting application and precious metals because of theirs cost. Electrorefining is also a part of processes in recycling of metals. It should be noted that large electrolytic plants for metal production are heavy consumers of electric energy1. In the metal electrorefining and electrowinning the main requirements are to produce pure and compact deposits. This is done at lower current densities. From qualitatively the same, but less concentrated solutions at higher current densities metal deposits in form of powder are obtained. Powder electrodeposition can also be treated as kind of electrowinning or electrorefining, which produces the metal deposits in forms suitable for sintering and various different applications.

*Electroplating* can be defined as a treatment that modifies the surface of a metal or occasionally a nonmetal, without changing its bulk properties, in order to improve the appearance of a surface, to increase the corrosion and abrasion resistivity, etc. The improving the appearance was the aim of electroplating earlier, now it is mainly the change of surface properties from those of substrate material to those of electroplated metal. Obviously, the coating can successfully change the surface properties of substrate only if it is compact and nonporous, as well as good adherent. Metal objects we meet in everyday life are often electroplated, but it seams that the most important application of electroplating technology is the manufacture of electronic components (circuit breakers and contacts). Electroplating can be performed from molten salts and aqueous and non-aquaeous solutions, depending on the nature of electrodeposited metal, but most frequently from aqueous solutions.

*Electroforming* is the manufacture of articles by electrodeposition. If deposit is good from electroplating point of view except adhesion, and can be removed from the cathode as an entity in itself, it has been electroformed. Electroforming is a branch of electroplating technology, but involve some additional steps, as for example the production, preparation and extraction of the master.

Electroless metal deposition and anodic oxidation of metals can also be include in the field of electrometallurgy.

Empirically is known what type of deposit can be obtained under specific conditions, however how and why this can be achieved still remains a mystery in some cases.

### 9.2.2 BASIC FACTS

### 9.2.2.1 Electrodes and electrochemical reactions, cell and circuit

In a metallic conductor free conduction electrons transport the charge whereas in an electrolytic conductor it is ions. In order to include an electrolytic conductor in an electrochemical circuit it is necessary to make electrical contacts to and from the electrolyte by metallic conductors. A metallic conductor immersed in an electrolyte solution is an electrode, and two electrodes connected electrolytically represent an electrochemical cell1. The simplest electrochemical circuit is shown in Fig.2

The electrochemical circuit consists of a current source, metallic connecting wires, an electrochemical cell, ohmic resistance, current and voltage measuring instruments and a circuit breaker. In technical practice more complicated circuits are used, but in principle all of them are the same as the one shown in Fig. 2.
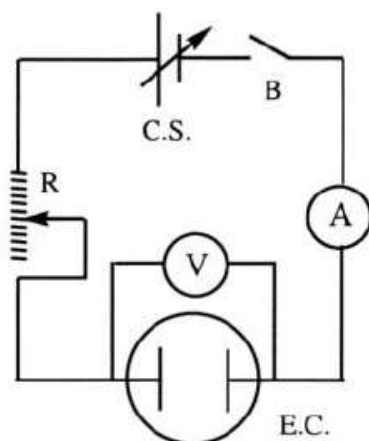


**Figure 2**. An electrochemical circuit. **C.S**.-current source, **R** -ohmic resistance, **V** - voltmeter, **A**-ampermeter, **E.C**- electrochemical cell, **B** - circuit breaker.

The electrochemical circuit consists of a current source, metallic connecting wires, an electrochemical cell, ohmic resistance, current and voltage measuring instruments and a circuit breaker. In technical practice more complicated circuits are used, but in principle all of them are the same as the one shown in Fig. 2.

Obviously, a steady current flow in the circuit from Fig. 2. can only be maintained if there is a change of charge carrier at the metal-electrolyte interface by a chemical transformation involving the transfer of electrons across the interface, i.e., by an electrochemical reaction. It constitutes the bridge between the current of electrons in the metallic part of the electrochemical circuit and the current of ions in the electrolytic part of the circuit.

### 9.2.2.2 The electrochemical double layer and possible electrochemical reactions

If the metal ions in the solution are the same as in the electrode metal lattice, or if the same substance is present in the electrolyte in two oxidation states, an electron transfer reaction can occur at the metal-electrolyte interface and lead to the development of a potential difference. Such an interface behaves like an electrical circuit consisting of a resistor and a capacitor in parallel. The electron transfer takes place until a dynamic equilibrium is reached. In the case of metal electrodes, depending on the system, this process begins with either the deposition of ions from solution onto the metal electrode or with the dissolution of the metal electrode. In equilibrium the electrode is more positive than the solution in the first case and more negative in the second one. A number of electrochemical reactions are possible at such an interface, as for example
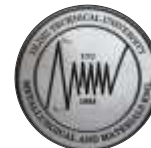
1. The reduction of metal cations to the metal and vice versa

$$Cu^{2+} + 2e^- \underset{\leftarrow}{\overset{\rightarrow}{}} Cu \tag{1}$$

2. The reduction of hydrogen cations to gaseous hydrogen and vice versa

$$2H^+ + 2e^- \underset{\leftarrow}{\overset{\rightarrow}{}} H_2 \tag{2}$$

3. The decrease of the oxidation state of the cations and vice versa

$$Fe^{3+} + e^- \underset{\leftarrow}{\overset{\rightarrow}{}} Fe^{2+} \tag{3}$$

4. The reduction of anions to metal and vice versa

$$[Cd(CN)_4]^{2-} + 2e^- \underset{\leftarrow}{\overset{\rightarrow}{}} Cd + 4CN^- \tag{4}$$

5. The reduction of molecules to anions and vice versa

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \; (in \; alkaline \; media) \tag{5}$$

6. The oxidation of molecules to cations and vice versa

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \; (in \; acid \; media) \tag{6}$$
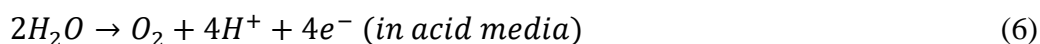

### 9.2.3 SELF DRIVING CELLS

### 9.2.3.1 The Nernst equation and energy producing cells

For the electrochemical reaction

$$O + ne^- \underset{\leftarrow}{\overset{\rightarrow}{}} R \tag{7}$$

where O is the oxidized state which accepts *n* electrons and R is the reduction state or the donor of electrons, in equilibrium, the Nernst equation is written in the form

$$E_{O/R} + E_{O/R}^\theta + \frac{RT}{nF} ln \frac{a_0}{a_R} \tag{8}$$

Where $E_{O/R}$ is the equilibrium electrode potential, $E_{O/R}^\theta$ is the standard electrode potential and $a_0$ and $a_R$ are the activities of the electron acceptor and donor, respectively[1,2].

In Table 1. the standard potentials for some electrode reactions are given.

**Table 1**. Standard potentials of metal deposition and dissolution reactions.

| Electrode reaction | Standard potentials, V | Electrode reaction | Standard potentials, V |
|---|---|---|---|
| $Li^+ + e^- = Li$ | -3.045 | $Co^{2+} + 2e^- = Co$ | -0.277 |
| $K^+ + e^- = K$ | -2.925 | $Ni^{2+} + 2e^- = Ni$ | -0.250 |
| $Na^+ + e^- = Na$ | -2.714 | $Sn^{2+} + 2e^- = Sn$ | -0.163 |
| $Mg^{2+} + 2e^- = Mg$ | -2.363 | $Pb^{2+} + 2e^- = Pb$ | -0.125 |
| $Al^{3+} + 3e^- = Al$ | -1.662 | $Cu^{2+} + 2e^- = Cu$ | 0.337 |
| $Zn^{2+} + 2e^- = Zn$ | -0.763 | $Cu^+ + e^- = Cu$ | 0.521 |
| $Cr^{3+} + 3e^- = Cr$ | -0.744 | $Ag^+ + e^- = Ag$ | 0.799 |
| $Cr^{3+} + 3e^- = Cr$ | -0.744 | $Ag^+ + e^- = Ag$ | 0.799 |
| $Fe^{2+} + 2e^- = Fe$ | -0.440 | $Au^{3+} + 3e^- = Au$ | 1.498 |
| $Cd^{2+} + 2e^- = Cd$ | -0.403 | $Au^+ + e^- = Au$ | 1.691 |

he signs of two electrodes connected to a cell can be determined by using the values of standard electrode potentials. Only, if they are close to each other the Nernst equation should be used to determine the polarity of them. The equilibrium potential difference for the cell

$$Zn|ZnSO_4, H_2O, H_2SO_4\|ZnSO_4, H_2O, H_2SO_4|Cu \qquad (9)$$
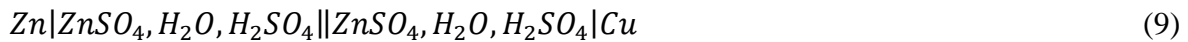
which is illustrated in Fig. 2.2, can be evaluated as follows.

Obviously, the equilibrium concentration of electrons in the more negative electrode will be larger than in the more positive one. According to Table 2.1, the possible reactions on the electrodes are:
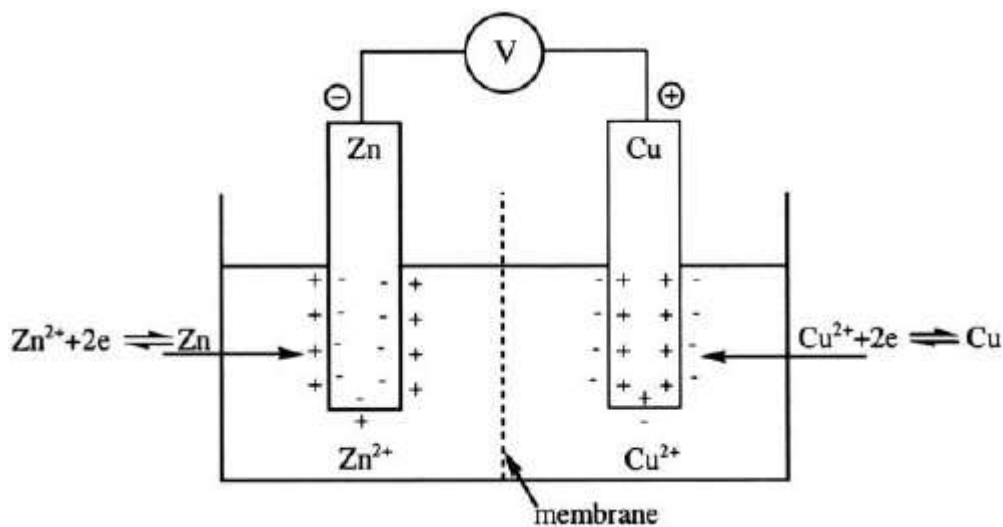


**Figure 2**. Schematic representation of a cell $Zn|ZnSO_4, H_2O, H_2SO_4\|ZnSO_4, H_2O, H_2SO_4|Cu$ in equilibrium. V is a high impedance voltmeter.

$$Zn \underset{\leftarrow}{\overset{\rightarrow}{}} Zn^{2+} + 2e^- \qquad E^\theta = -0.763\,V \qquad (10)$$

and

$$Cu^{2+} + 2e^- \underset{\leftarrow}{\overset{\rightarrow}{}} Cu \qquad E^\theta = -0.763\,V \qquad (11)$$
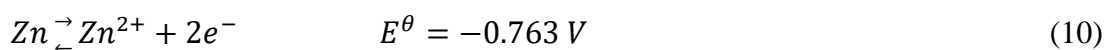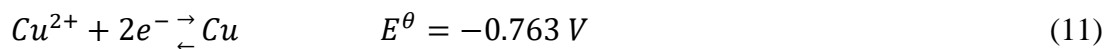
The equilibrium potential difference $E$ is given by

$$E = \left(E^\theta_{Cu^{2+}/Cu} + \frac{RT}{2F} ln a_{Cu^{2+}/Cu}\right) - \left(E^\theta_{Zn^{2+}/Zn} + \frac{RT}{2F} ln a_{Zn^{2+}/Zn}\right) \qquad (12)$$

If the electrodes are connected as in Fig. 3, the reaction on the electrodes are:

$$Zn \rightarrow Zn^{2+} + 2e^- \qquad (13)$$

and

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad (14)$$

The overall reaction in is then:

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+} \qquad (15)$$

Obviously, oxidation will take place on the more negative electrode, making it an electron sink, and reduction will occur on the more positive electrode, making it an electron source.

Such electrochemical transformations at the two interfaces provides a steam of electrons available for external use, which is the essence of energy producing cells (electrochemical power sources).
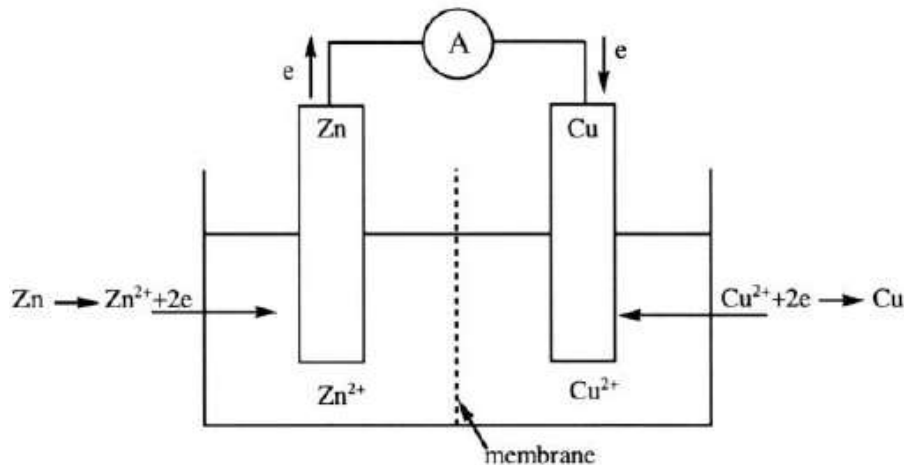


**Figure 3**. The cell $Zn|ZnSO_4, H_2O, H_2SO_4\|ZnSO_4, H_2O, H_2SO_4|Cu$ as an energy producer. A is the low impedance ampermeter.

Reaction, given by Eq. 15 will go from left to right until the potentials of the electrodes become equal, which corresponds to the zero cell voltage and equilibrium activities $a_{e,Zn^{2+}}$ and $a_{e,Cu^{2+}}$ of zinc and copper ions, respectively. It follows then from Eq. 12 that if $E = 0$

$$E^{\theta}_{Cu^{2+}/Cu} - E^{\theta}_{Zn^{2+}/Zn} = \frac{RT}{2F} ln K^{\theta} \tag{16}$$

where

$$K^{\theta} = \frac{a_{e,Zn^{2+}}}{a_{e,Cu^{2+}}} \tag{17}$$

represents the equilibrium constant for reaction 15. The value of $K^{\theta} \sim 10^{37}$ means that the $Cu^{2+}$ ions can be completely removed from the electrolytic solution by reaction 15.

### 9.2.3.2 Cementation

If a piece of zinc is immersed in a copper sulfate solution the reaction 13 occur at one local area of the electronic conductor and reaction 14 at another local area. Reaction 13 and 14 occur spontaneously, and the overall reaction is given by Eq. 15. The system is self-driven and produces power, but the corresponding electrochemical energy is unavailable because the two interfaces are short-circuited. This reaction is used in purification of zinc sulphate solution from more positive metallic ion impurities in zinc electrowinning process.

### 9.2.3 ELECTROLYSIS

### 9.2.3.1 Decomposition voltage

The self-driving cell from Fig. 3 can be rearranged to a driven cell by connecting the power supply in the circuit as shown in Fig. 4.

The reactions on the electrodes will be

$$Zn^{2+} + 2e^- \rightarrow Zn \tag{18}$$

and

$$Cu \rightarrow Cu^{2+} + 2e^- \tag{19}$$

and the electron steam will flow in the opposite direction to that in the same cell working as a self driven one only if the power supply voltage is larger than the equilibrium potential difference of the same cell, working as a self driven one.
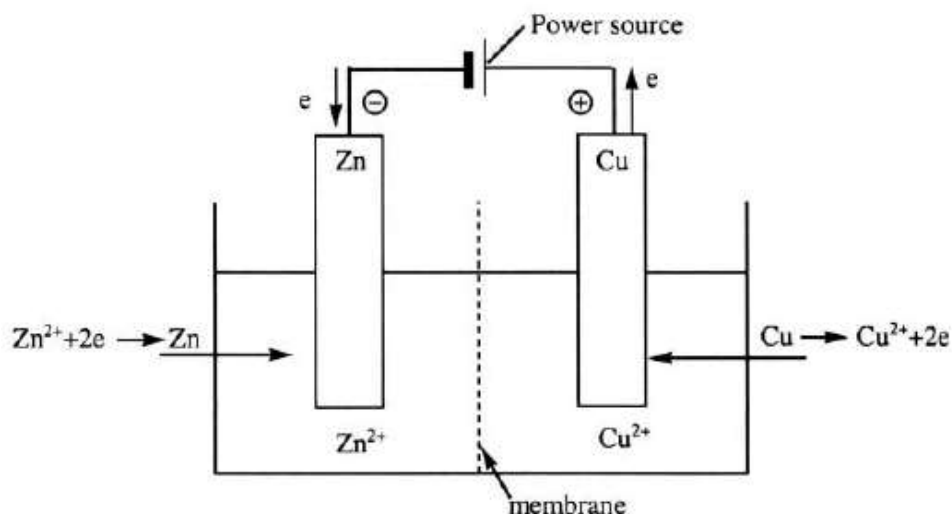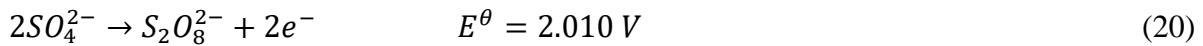


**Figure 4**. Schematic representation of the cell $Zn|ZnSO_4, H_2O, H_2SO_4 \| ZnSO_4, H_2O, H_2SO_4|Cu$ as a driven cell.

If two or more anodic and cathodic reactions are possible in some driven cell, the reactions with the lowest equilibrium potential difference will take place on the electrodes first. This means that the reaction with the most positive equilibrium potential will take place first on the cathode (the electrode connected with the negative terminal of power supply, at which reduction occurs), and the reaction with the most negative equilibrium potential on the anode (the electrode connected with the positive terminal of the power supply, at which oxidation occurs). It is important to remember that the terms anode and cathode are connected with the nature of the reaction (oxidation or reduction) at the electrode and not with their polarity. Thus, in a self driven cell, the anode is the negative terminal and the cathode is the positive terminal of the cell, a situation which is precisely the opposite of that which exists in an externally driven cell.
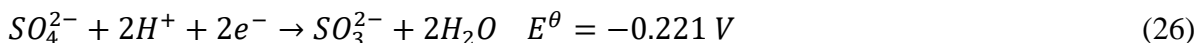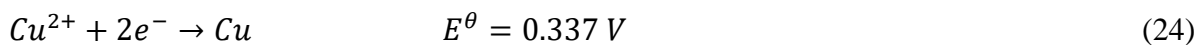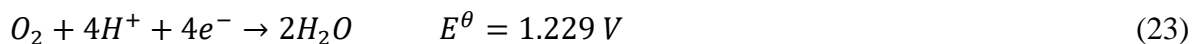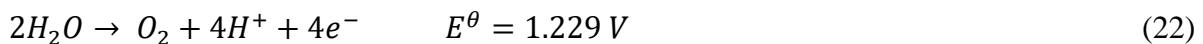
### 9.2.3.2 A cell with an insoluble anode

In the driven cell: $(-)Cu|CuSO_4, H_2SO_4, H_2O|Au(+)$ the following reactions on **the anode** (**Au**) are possible:

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \qquad E^\theta = 2.010\ V \tag{20}$$

$$Au \rightarrow Au^{3+} + 3e^- \qquad E^\theta = 1.498\ V \tag{21}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^\theta = 1.229\ V \tag{22}$$

and **on the cathode (Cu)**

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^\theta = 1.229\ V \tag{23}$$

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^\theta = 0.337\ V \tag{24}$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^\theta = 0.000\ V \tag{25}$$

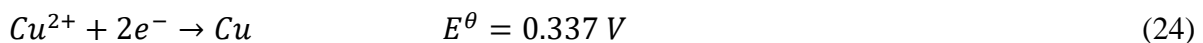$$SO_4^{2-} + 2H^+ + 2e^- \rightarrow SO_3^{2-} + 2H_2O \quad E^\theta = -0.221\ V \tag{26}$$
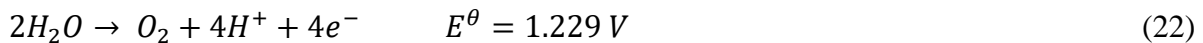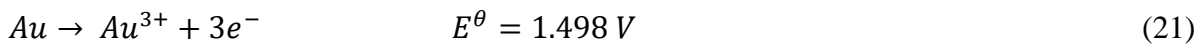
According to the rule derived in the conclusion from section 2.3.1, on the anode the oxygen evolution reaction will occur, and on the cathode copper ions will be reduced to the metal phase, because the most positive catodic reaction can be neglected due to the low oxygen concentration in the electrolyte solution. Hence the reaction:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^\theta = 1.229\ V \tag{22}$$

will take place at the anode and the reaction

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^\theta = 0.337\ V \tag{24}$$

at the cathode.

Obviously, the minimum external cell voltage for electrolysis to occur in this case is 0.893 V.

The overall reaction in the cell is

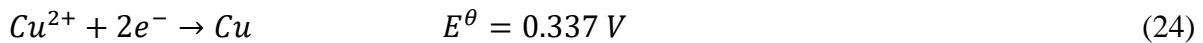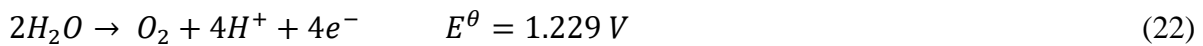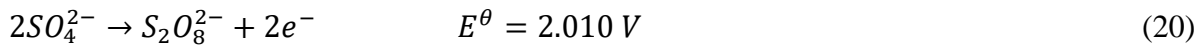$$2Cu^{2+} + 2H_2O \rightarrow 2Cu + O_2 + 4H^+ \tag{25}$$

It follows from the Eq. 25 that in a cell with an insoluble anode the concentration of depositing ions decreases and the hydrogen ion concentration increases during electrolysis. The mechanism of the extraction of metals from ionic solutions and the essence of the electrowinning process are well explained by Eq. 25.
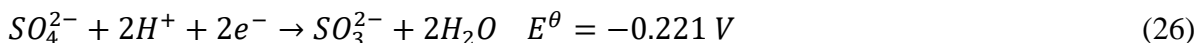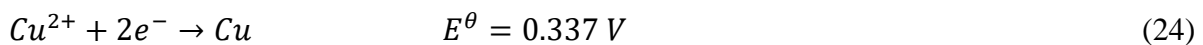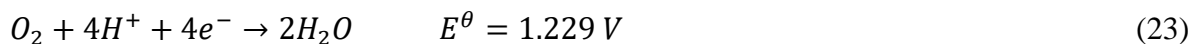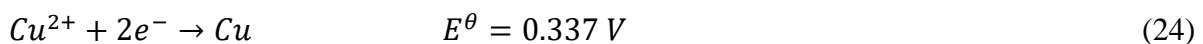
### 9.2.3.3 A cell with a soluble anode

In the cell: $(-)Au|CuSO_4, H_2SO_4, H_2O|Cu(+)$ the following reactions are possible on the anode (**Cu**):

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \qquad E^\theta = 2.010\ V \tag{20}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^\theta = 1.229\ V \tag{22}$$

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^\theta = 0.337\ V \tag{24}$$

and **on the cathode (Au):**

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^\theta = 1.229\ V \tag{23}$$

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^\theta = 0.337\ V \tag{24}$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^\theta = 0.000\ V \tag{25}$$

$$SO_4^{2-} + 2H^+ + 2e^- \rightarrow SO_3^{2-} + 2H_2O \quad E^\theta = -0.221\ V \tag{26}$$

Hence, the reaction

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^\theta = 0.337\ V \tag{24}$$

occurs on the anode, and

$$Cu \rightarrow Cu^{2+} + 2e^- \qquad E^\theta = 0.337\ V \tag{19}$$

at the cathode, and so the composition of the electrolyte solution remains constant if the anode is made of pure copper and oxygen is removed from the solution. The lowest cell voltage at which electrolysis can start in this cell is zero.

It is obvious that electrorefining processes are based on electrolysis in cells with soluble anodes.

### 9.2.3.4 Current efficiency

Metal deposition can be accompanied by any other cathodic reaction, most frequently hydrogen evolution. This leads to the situation in which metal is deposited but metal deposition uses only a part, $I_{Me}$ of the total current, $I$, through the cell. The current efficiency

$$\eta = \frac{I_{Me}}{I} \tag{27}$$

indicates which part of the total current is used for the deposition of metals. It is a very important parameter of an electrodeposition process.
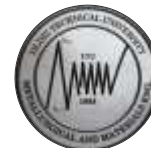
### 9.2.3.5 Faraday's law

Faraday's law relates the quantity of electricity passed through the cell and the quantity of chemical substances which react on the electrodes. It states that the mass of metal, *m,* electrodeposited on the cathode is given by

$$m = \frac{ItM}{nF}\eta_I \tag{28}$$

where $I$ is the total current, $t$ is the deposition time, $M$ is the molar mass of the deposited metal, $\eta_I$ is the current efficiency and $nF$ is the number of Faradays per mole of consumed ions. It follows from Eq. 28 that can be easily determined by measuring the electrodeposited mass of metals and supplied quantity of electricity.

## 9.3 EQUIPMENT AND MATERIALS

**Apparatus:** Eye protection, Beaker (250 cm3), Stainless steel plate cathodes and one hard lead plate anode electrodes (about 5 mm diameter),2 Retort stand and clamp to hold electrodes, DC power supply (6 volt), Leads and crocodile clips 4.

**Chemicals:** Aqueous copper(II) sulphate, about 0.5 M, 200 cm$^3$

## 9.4 EXPERIMENTAL PROCEDURE

**Electrolysis** is the chemical process of using an electrical current to stimulate non-spontaneous reactions. A **non-spontaneous reaction** is one that needs energy to work while it proceeds. In other words, the process would not happen on its own, as it goes in an unfavourable, or a reversed, direction.

Important uses include its role in separating metals from a natural source, such as our friend the copper ore. Other useful benefits for electrolysis include the purification of metals and decomposition of compounds like water.

The site where electrolysis occurs is in an **electrolytic cell**, which is a type of electrochemical cell that drives an electrical current using a non-spontaneous reaction. So, not like a cell in your body, but a container. Thus, these cells must have an energy source to drive the reaction in the reverse or opposite direction, like a battery. Be careful not to confuse an electrolytic cell with electrolysis. Always remember that the electrolysis process is performed using an electrolytic cell.

### How Does Electrolysis Work?

We can understand the process of electrolysis by looking at an example involving the purification of a copper metal. This process will require an **anode**, a positively charged electrode, and a **cathode**, a negatively charged electrode. In this case, an impure copper metal is the anode, while the pure copper metal is the cathode. The goal is to use electrolysis for the purpose of recycling a dirty old piece of copper pipe, or impure copper, to a beautiful, purified copper pipe.
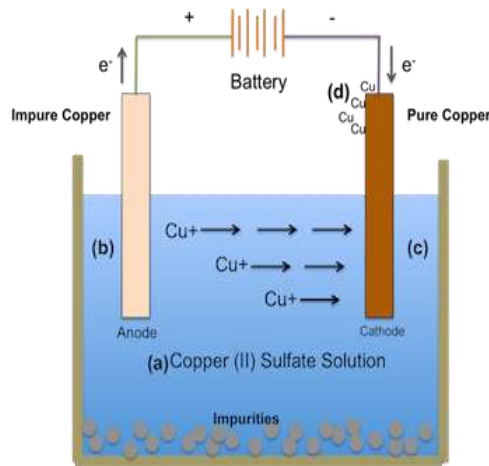
**Figure 5**. Schematic representation of copper (II) sulphate solution electrolysis cell.

The copper sulfate **electrolyte**, or solution, ensures there is a liquid medium conducive for ion movement inside the cell (a). When copper ions leave the impure copper pipe through the help of an energy supply, they migrate from the anode (b) to the cathode (c). After reaching the cathode, they collect the electrons needed to form a neutral, or no charge, copper metal. These neutral copper metal atoms gather on the pure copper cathode (d). The leftover impurities from the anode, or the ones not traveling to the cathode to be purified, collect at the bottom of the cell.

In the experiment copper sulfate solution is prepared at a concentration of 25 g / ml to be used instead of the copper leaching solution. The prepared solution is divided into equal amounts in two separate beakers. Anode and cathode plates are prepared with two pre-cleaned and prepared stainless steel plate cathodes and one hard lead plate anode. Cathode plates are weighed with a precision scale before the experiment and their weights are noted. A cathode and an anode plate prepared for each experiment are immersed in solution parallel to each other and current is supplied to the prepared system from the power supply.

Two experiments are performed in which all parameters except the current intensity are kept constant (duration: 15 min, concentration: 25 g / ml Cu2SO4). At the beginning of the experiments, the system is applied in such a way that the amount of current is 0.1 A and the second is 0.2 A. Thus, it is tried to observe the effect of the applied current amount on the amount of copper obtained.

Both experiments are carried out for 15 minutes, then the copper deposited cathode plates are dried and finally weighed. As a result of the test, the amount of copper deposited is calculated from the difference between the initial and final weights of the cathode plates obtained as a result of each test.

## 9.5 ASSIGNMETNS AND REQUESTS

Determine the amount of copper deposited at the cathode plates.

## 9.6 REFERENCES

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2. YTÜ Metalurji Müh., "Demir Dışı Metal Üretimi Laboratuar Kitapçığı", 1997

3. BOR,F.Y., "Ekstraktif Metalurji Prensipleri Kısım II", Birinci Baskı, 1989

## 10. PRODUCTION OF COMPOSITE MATERIALS

### 10.1 OBJECTIVE

Production of E-Glass fiber reinforced composite plates with plastic matrix and fracture analyzes by performing impact test on samples taken from these plates.

### 10.2 THEORY

The new material group formed by at least two different materials via forming an interface in between without creating chemical bond is called composite. Basically, composite materials have two main components.

The matrix phase forms the main component of the composite material. Its main task is to hold the structure together stably by covering around the reinforcement (fiber) component. Another task is to transfer and distribute any applied force to the reinforcement phase through the interface bond without being destroyed. An ideal matrix material should be able to coat the fibers very well by surrounding them properly.

In the composites the load-bearing main element is the reinforcement fibers. The most commonly used and cost-effective reinforcement type is the glass fiber. Aramid and carbon fibers are both reinforcement types with high mechanical properties and expensive. Reinforcements are also available in different ways. Figure 1 shows the classification of composites according to their reinforcement shape and distribution. Figure 2 illustrates the conditions of these species within the structure. Figure 3 shows different weaving types.
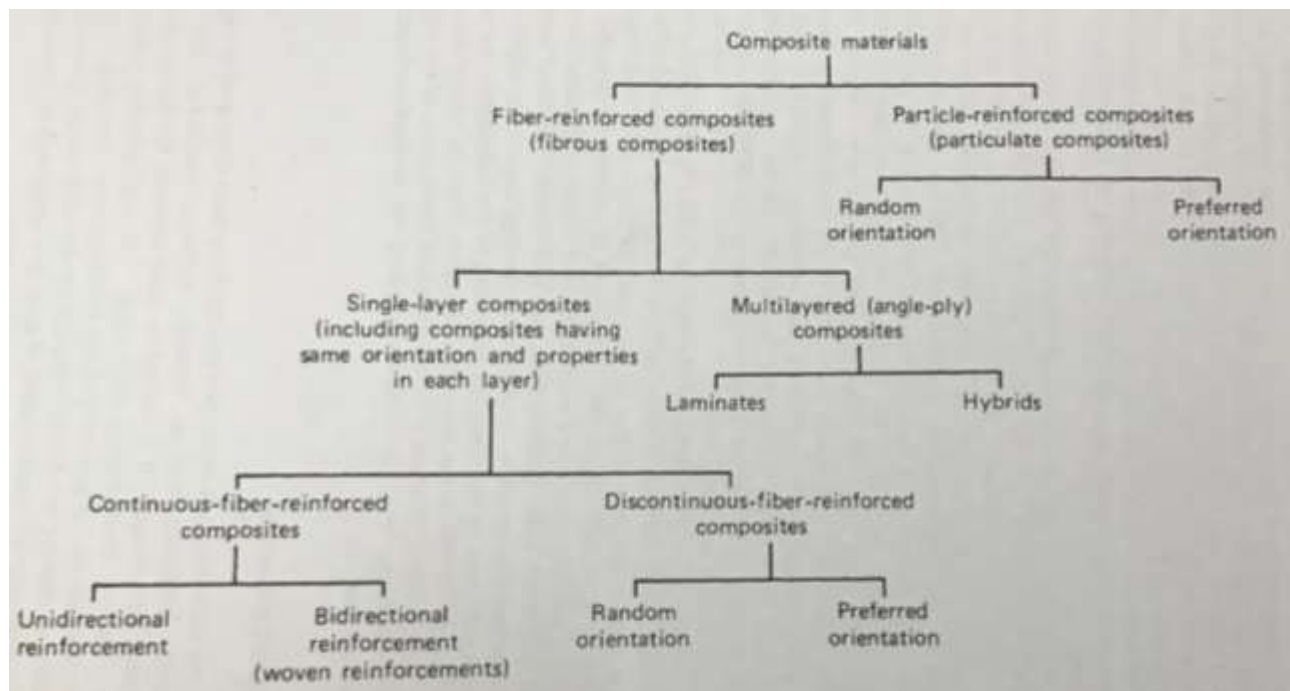


Figure 10.1 Classification of composites according to reinforcement shapes and distributions
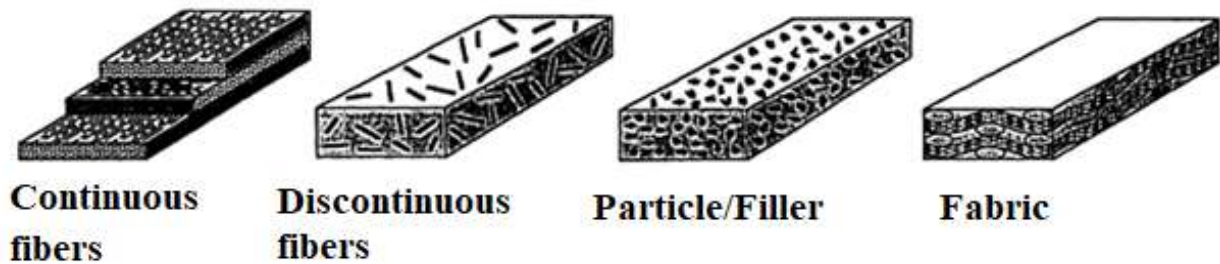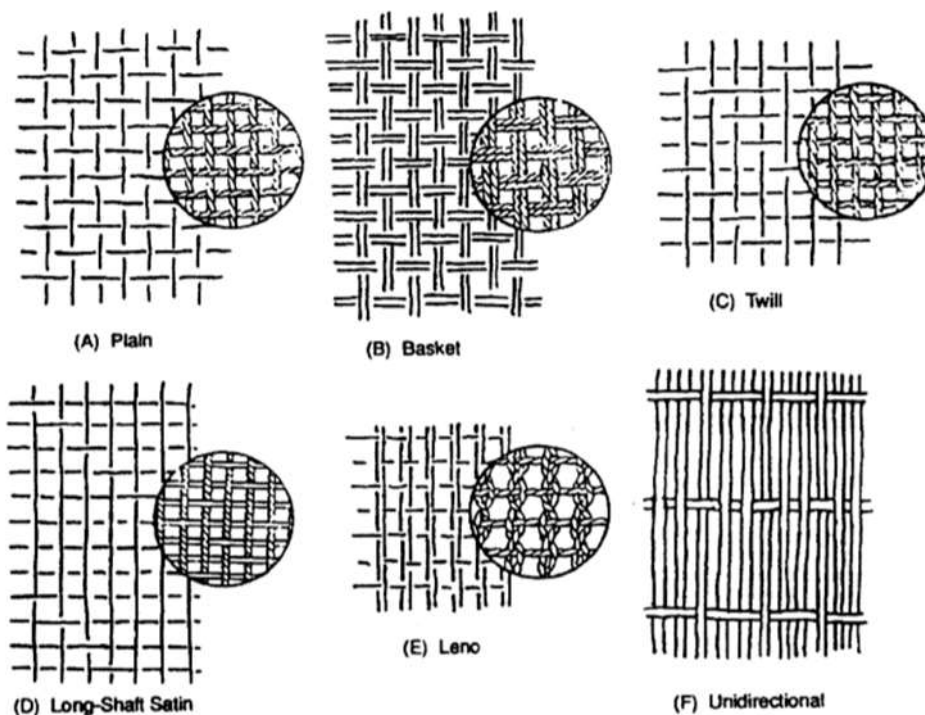
Figure 10.2 Various reinforcement types



Figure 10.3 Various woven fabric types

## 10.2.1 Grouping of Composite Materials by Matrices

• Plastic Matrix Composites (PMCs): It is the most widely used composite type today. It has approximately 80% utilization rate in all composites. They can be reinforced with continuous or discontinuous fibers, or they can be reinforced with particles.

• Metal Matrix Composites (MMCs): It is the most used group after plastic matrix composites. Metal matrices, which are generally used as particle-reinforced, have applications in where wear resistance is required. In addition, honeycomb structure produced from aluminum is included in this group.

• Ceramic Matrix Composites (CMCs): They are not widely used. Unlike other groups, it has a brittle matrix. Composites in this group are reinforced with ductile fibers to increase the toughness of the brittle matrix.

## 10.2.2 Plastic Matrix Composite

Plastic matrix is the most widely used composite type with many advantages. Therefore, it is important to know the plastic to learn the properties of the composite. Plastics consists of repeating of molecules of simple molecules formed by carbon, hydrogen, oxygen, nitrogen and other organic or inorganic elements. The plastic matrix is generally divided into two groups:

a) Thermosets: Epoxy, polyester, vinylester, phenolic resins

b) Thermoplastics: PE (polyethylene), PP (polypropylene), PS (polystyrene), PET (polyethylene terephthalate), PBT (polybutylene terephthalate), PA (polyamide), PPS (polyphenylene sulfide), PEEK (polyether ether ketone)…

According to the reinforcement, a classification can be made as follows:

- Plastic-Plastic Composites
- Plastic-Metal Composites
- Plastic-Ceramic Composites
- Plastic-Foam Composites

## 10.2.3 Production Methods of Plastic Matrix Composites

*Hand Lay-Up Method:* It is the most widely used method for the production of large-scale thermoset matrix composites. After the release agent is applied, the gelcoat is applied. After the gelcoat layer has hardened, thermoset resin and mat or woven fiber fabrics are applied with a brush or roller, respectively. With hand lay-up, which is a low cost method, a reinforced plastic product can be obtained with a fiber volume ratio of 25-35%. Since it is a labor-intensive production method, capacity depends on the number of labor and molds. An average of 2 products can be taken per day from a mold.

*Spray-up Method:* It is a molding method that enables the hand lay-up method to be applied more rapidly. During production, resin and fiber are sprayed on the mold with the help of a special machine, called as spray gun. In the spraying method, the continuous fiber bundle is used by chopping 17-50 mm in length during the spraying process. It provides mass production opportunity and labor saving in large surface products.

*Vacuum bagging and autoclave:* These are the methods applied to increase the properties of the composite after hand lay up or spray up methods. A vacuum blanket is placed on various separation fabrics to absorb excess resin on resin composite products that have not been cured in vacuum bagging. A heat-resistant film called vacuum bag is placed at the top by attaching a vacuum nozzle and is closed with a special paste to ensure impermeability. The system is put into vacuum and vacuum continues to be applied until the curing process is complete. Excess resin is passed through the product, increasing the fiber volume ratio, thinning the section and reducing the weight, eliminating the voids and increasing the mechanical properties as a result. Similarly, in the autoclave, uncured products are vacuumed by taking the vacuum bagging system. Then, curing is achieved by giving heat and pressure in autoclave chambers.

*Vacuum infusion:* Mat or woven fiber fabrics are placed on top of each other and taken to the vacuum bagging system. However, in the vacuum bag, in addition to the vacuum inlet, the openings through which the resin will enter are opened. As the system is put into vacuum, the resin starts to fill into the inside of the bag and wets the fibers to form the composite.

*RTM (Resin Transfer Molding):* In this production method, two-sided smooth products are obtained by using two molds, male and female. Fiber fabrics are placed on the mold and the molds are closed. Thermoset resin is injected into the mold under pressure from a pre-prepared resin injection point. With the resin injection method, a higher quality product is obtained more quickly and economically than hand laying.

*SMC/BMC (Sheet Mold Compound/Bulk Mold Compound):* It is a method of forming fiber, resin and filling material mixtures in hot press molds at 150-170°C and 50-120 kgf/cm$^2$ pressure. Complex shaped products can be obtained. It is a fast and rapid method of 3-6 minutes. In SMC, pulp formed by pre-combining long clipped (25-50 mm) fibers with filler and resin is used, while in BMC, a dough formed by the combination of short cropped (3-12 mm) fiber, filling and resin is used.

*Filament winding:* It is a molding method used especially for the production of pipes and tanks. It is in the form of winding continuous fiber bundles on a rotating mold at certain angles after wetting from the thermoset resin bath.

*Centrifugal casting:* It is used in the production of cylindrical products such as pipes, tanks, poles. The chopped fiber and thermosetting resin are sprayed together into a rotary die. The centrifugal force resulting from the rotation of the mold ensures that the laminate adheres to the mold surface and obtains a smooth product on both sides.

*Pultrusion:* It is based on the principle that continuous fiber bundles are hardened while being drawn through a hot mold in the desired profile after passing through a thermoset resin bath. In the direction of fiber reinforcement, very durable profile products with a very high glass fiber content are obtained.

*Termoplastic injection/extrusion:* While extrusion machines are used for molding profile type products, injection machines are used for molding complex shaped products. In injection and extrusion machines operating with the same principle, the granular thermoplastic raw material supplied from the feeding chamber is heated in the heating zone, making it fluid, and short-cropped fiber is fed on the one hand. Then, a homogeneous mixture is provided with the auger grooves on the one hand, and it is carried towards the outlet end on the other hand. In extruders, profiles are drawn in accordance with the mold shape with the help of pressure effect and pulling apparatus through the mold placed at the outlet end, while in injection machines, short clipped fiber mixed with fluidized thermoplastic is injected into the closed mold located right next to the exit nozzle, and it is cooled and hardened in a closed mold.

### 10.2.4 Glass Fiber Production

Glass fiber is produced from conventional glass production raw materials such as silica, colemanite, aluminum oxide, soda, magnesium oxide. The raw material is finely ground and mixed to obtain a homogeneous mixture and fed to a melting furnace operating at about 1600 ° C. Here, the mixture slowly becomes liquid. With a winding system suitably placed in the process, a high velocity of 50-70 m/s and a 5-20 micron diameter glass fiber are collected on a bobbin by winding on the mandrel, depending on the type of application.
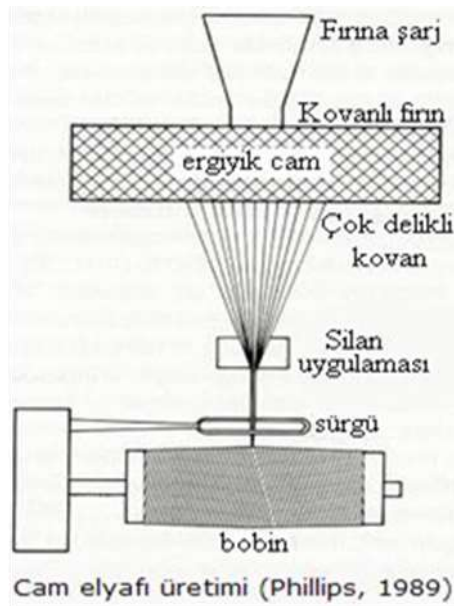


Figure 11.4 Schematic figure of glass fiber production

The glass fibers are coated with a chemical composition, called a binder, before being bundled. The type of binder is one of the most important factors affecting the performance of glass fiber in the composite material. The strength of the composite is proportional to the strength of the resin-glass bond. The strength of this bond depends on the type of binding groups in the binder used. The binder consists of a mixture of "film-forming", "binding groups", "antistatic additive", "plasticizer" "lubricant" materials.

### 10.3 USED STANDARDS

TS EN ISO 179-1: Plastics - Determination of Charpy impact properties - Part 1: Impedance impact test

### 10.4 USED DEVICES AND MATERIALS

- Fiber reinforced composite samples according to test standards
- Digital caliper
- Impact device

## 10.5 EXPERIMENT

### 10.5.1 Materials

- Fiber Material: E-glass woven or mat fabric
- Matrix material: Orthophthalic based unsaturated polyester resin
- Resin accelerating agent: Cobalt octoate
- Resin initiating agent: Methyl Ethyl Ketone (MEK) Peroxide
- Dosing pipettes (Pasteur Pipettes)
- Mixing Cup
- Mold
- Mold release agent
- Brush and/or roller
- Acetone or thinner
- Plastic glove

### 10.5.2 Application

1. The mold release agent is applied to mold and left to dry.
2. The reinforcing material to be used is cut into appropriate sizes and its weight is measured.
3. Four times amount of resin is prepared in a mixing cup by mixing with accelerator and the initiating agent at a required ratio. (The accelerator and initiator should not be placed at the same time because they react violently with each other!)
4. Apply a small amount of resin with a brush onto the dried mold release agent.
5. A layer of reinforcing fabric is placed on it.
6. Resin is applied by light pressure on the reinforcing fabric with brush.
7. Put the second layer of reinforcing fabric and repeat the process until required thickness is obtained.
8. Wait until the resin is cured.
9. Clean the brushes, cups and pipettes with acetone.

## 10.6 OBTAINING RESULTS

The dimensions of the samples in different layer thicknesses will be measured and the cross-sectional area will be calculated by taking minimum values from three measurements. Each student will do this by using a digital caliper. The test shall be carried out by placing the sample on impact device. Impact energy will be measured, samples will be compared and the fracture type will be examined.

## 10.7 CALCULATION

Impact energy will be measured in joule (J) unit and will be divided by the cross-sectional area of the sample.

## 10.8 CONCLUSION

The production steps of the composite parts will be observed in details. Materials with various layers thicknesses will be compared. At the end of the experiment, fracture analysis will be done.

## 10.9 INFORMATION REQUIRED IN THE EXPERIMENT REPORT

1. Definition, classification, types and examples of composite materials.
2. General information about plastic materials used as matrix materials, types, examples.
3. Short information about the production methods of plastic matrix composite materials.
4. General information about glass fibers.
5. Identification of materials used.
6. Application of composite production.
7. Calculation of the impact strength.
8. Comparison of the results of the samples.
9. Fracture analysis.
10. Specifying the sources used at the end of the report.

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