



T.C.

YILDIZ TECHNICAL UNIVERSITY

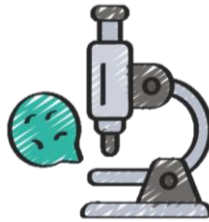
FACULTY OF CHEMISTRY AND METALLURGY

METALLURGY AND MATERIALS ENGINEERING DEPARTMENT

2022-2023 FALL

MSE3961 LABORATORY-I

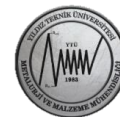
EXPERIMENT BOOKLET





CONTENTS

CONTENTS	i
SAFE WORKING PRINCIPLES IN LABORATORY	ii
1. MECHANICAL TESTS	1
2. CASTING EXPERIMENT	13
3. METALLOGRAPHY EXPERIMENT	22
4. CORROSION EXPERIMENT	29
5. POWDER METALLURGY EXPERIMENT	34
6. HYDROMETALLURGY EXPERIMENT	40
7. HEAT TREATMENT EXPERIMENT	45
8. CERAMICS EXPERIMENT	49
9. OPTICAL PROPERTIES OF MATERIALS	52
10.PYROMETALLURGY EXPERIMENT	61
11.POLYMER EXPERIMENT	71
NOTLAR	76



SAFE WORKING PRINCIPLES IN LABORATORY

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.
3. 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.
4. No food and beverage should not be consumed in the laboratory, and the face should not be touched while working
5. 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.
6. In the laboratory, movements that distract others should be avoided. Gaming or joking is strictly dangerous and forbidden in the laboratory.
7. Laboratory notebook should be kept for the studies conducted in the laboratory. Studies and observations must be recorded in this notebook.
8. Taps, gas valves and switches, should be kept closed when not in use.
9. Metallic laboratory tools should not be kept wet to avoid rusting.
10. The solid materials to be dispensed should be dropped into the designated waste bin in the laboratory.
11. Any incident occurred in the laboratory should be immediately notified to the administrators of the laboratory.
12. No substance or material should be taken out of the laboratory without the permission of the laboratory's administrators.
13. After use, each item should be cleaned according to the method of the appliance. Hands should be washed after leaving the laboratory.
14. Before using the microscope, the objective and ocular should be carefully cleaned with a cloth before and after each use without damaging the lens.
15. While diluting the acids and alkalis, they should always be poured slowly over the water, never the opposite.
16. 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.
17. When dealing with electricity, hands and electric switches and sockets must be dry. Electrical plugs should not be pulled out from the cord.

1. MECHANICAL TESTS

PART 1.1: HARDNESS TESTING

1.1.1 AIM

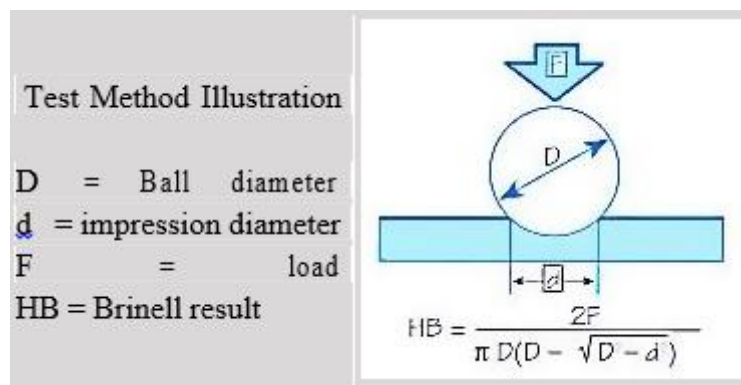
To introduce the principles of indentation hardness testing, emphasizing the limitations and significance of the results.

1.1.2 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,



where D is the diameter of the indenter ball and d is the average diameter of the indentation, both in mm.

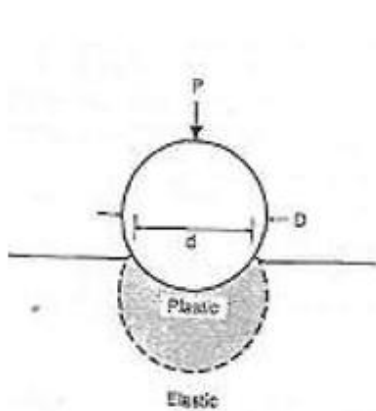


Figure-1: Geometry of deformation under a Brinell hardness indenter.

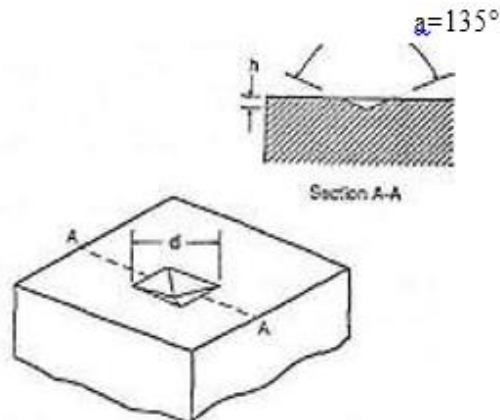


Figure-2: Vickers hardness indentation.

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° 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

$$\text{VHN} = \frac{1.8544P}{d^2} \quad (\text{in some sources VHN is cited as DPH})$$

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° 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-I 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.

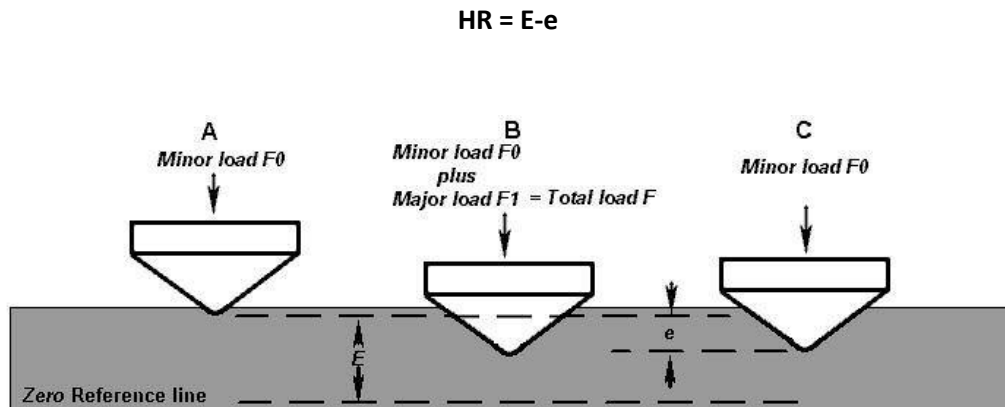


Figure 3.3: Increasing depth of penetration in the Rockwell test

Table 3.1: 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, for steels UTS can be **roughly estimated** from Brinell hardness as follows:

$$UTS \text{ (in MPa)} = 3.45 \times \text{BHN}$$

1.1.3 EQUIPMENT

Rockwell hardness tester

Brinell hardness tester

Microhardness (Vickers) tester

Different test specimens



1.1.4 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

1.1.5 ANALYSIS

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

1.1.6 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 indenter much greater than the yield stress? How much greater is it?

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

1.1.7 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 1.2: TENSILE TEST AND ANALYSIS OF MECHANICAL PROPERTIES OF A METAL

1.2.1 SUBJECT: Tensile testing and evaluation of tensile properties of materials.

1.2.2 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)

1.2.3 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, $A_0 = W_0 \cdot T_0$



Initial volume, $V_0 = A_0 \cdot L_0$

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 = $\frac{L_f - L_0}{L_0} \times 100$
- v. % Reduction of area = $\frac{A_0 - A_f}{A_0} \times 100$
- vi. Value of the strength constant, K , and the strain hardening coefficient, n , in the plastic region using:



MSE3961 Laboratory-I Experiment Booklet



$$s_T = K \epsilon^n$$

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

$$E = \Delta L / L_0$$

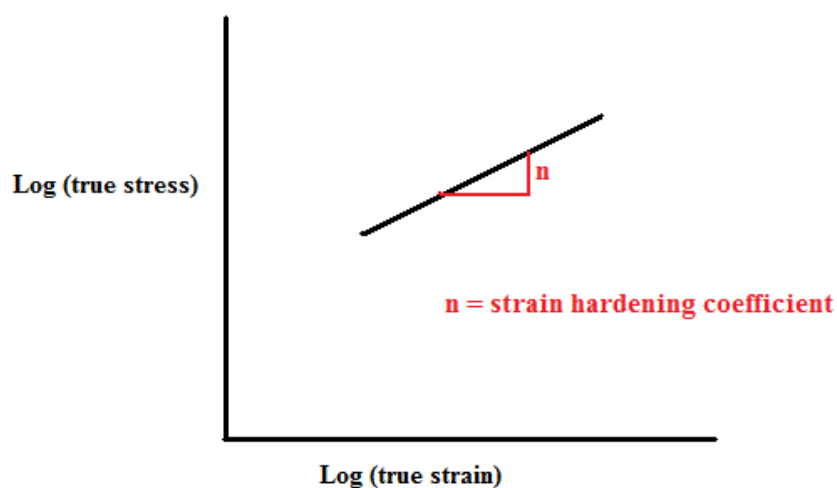
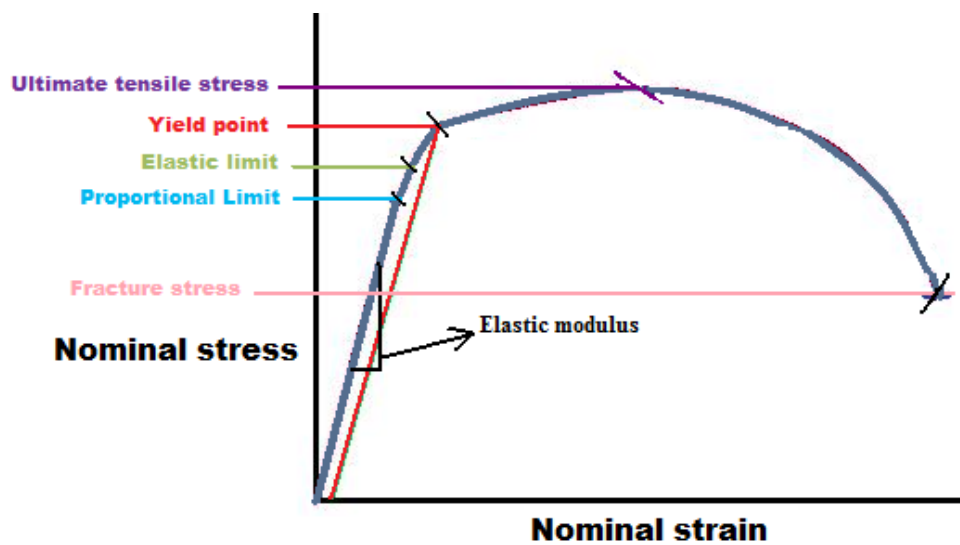
Actual Area = $V_i / (L_i + \text{Elongation})$

Nominal stress = Load / A_0

Nominal strain = Elongation / L_0

True stress = Load / Actual area = F/A_0

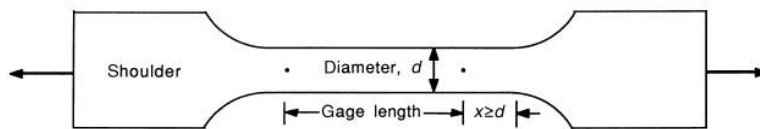
3. Draw a graph between Nominal stress (y-axis) and Nominal strain (x-axis); Log (True stress) (y-axis) and Log (True strain) (x-axis), from which the following can be calculated. Sample graphs are shown below:



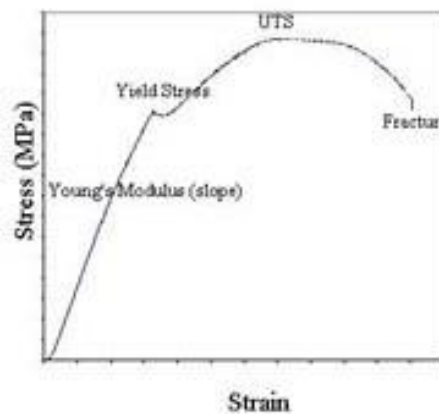
Note: Actual stress and true stress are the same; actual strain and true strain are the same.



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



1.2.4 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 1.3: IMPACT TESTING

1.3.1 OBJECTIVE

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

1.3.2 EQUIPMENT

Coolants

Standard Charpy V-Notched Test specimens

Impact tester

1.3.3 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,

$$E = m.g.(h-h')$$

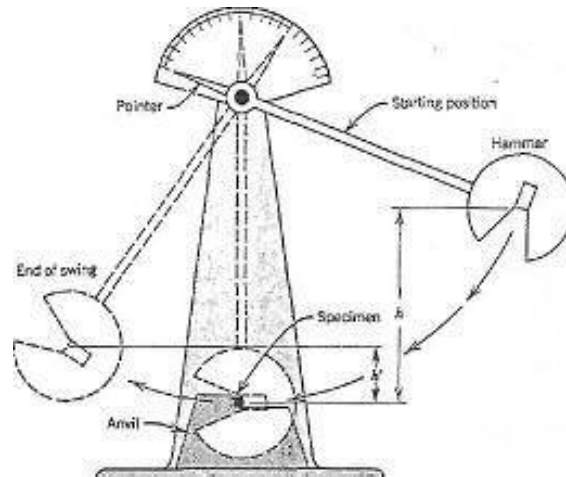


Fig. 1. Apparatus for impact testing of materials.

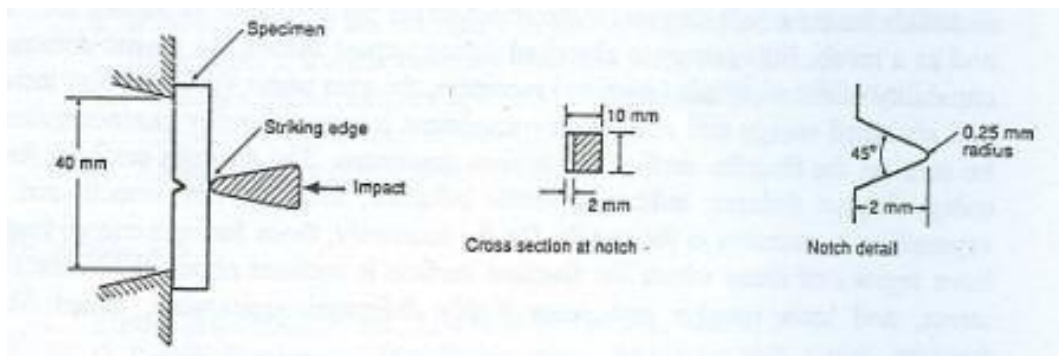


Fig. 2. Specimen and loading configuration for Charpy V-notched impact test.

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.

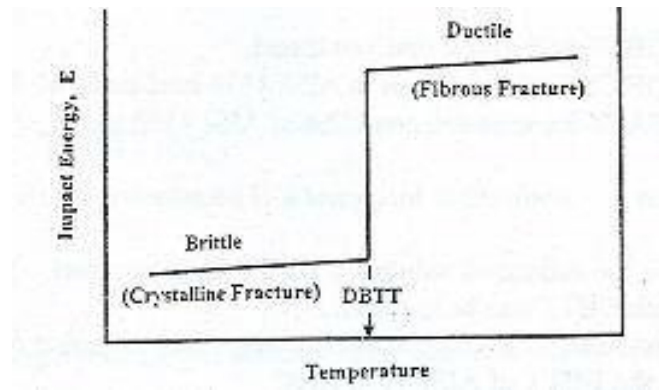


Fig. 3. Typical ductile-brittle transition curve for annealed low carbon steel.

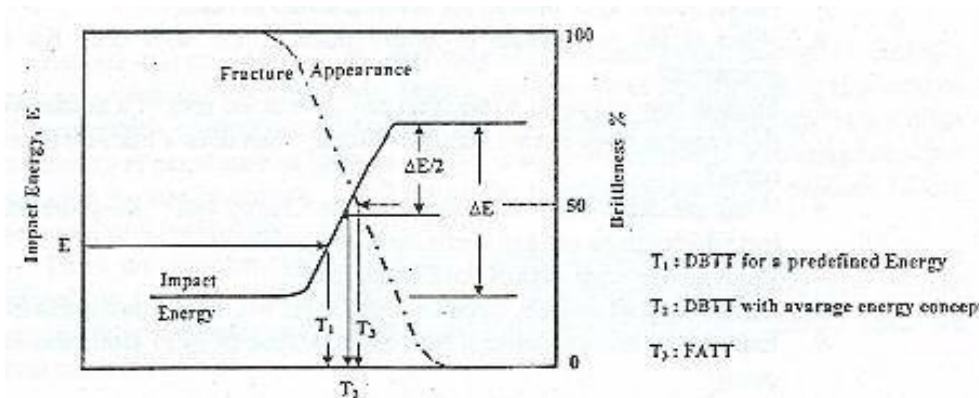


Figure-4: Various criteria of transition temperature obtained from Charpy tests.

1.3.4 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.

1.3.5 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 DBTT 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.
5. ASM Metals Handbook, 9th ed. Vol. 12.

2. CASTING EXPERIMENT

Aim

The purpose of this experiment is to introduce the casting method in general, to give information about the casting processes and to give hand skills about the production of sand molds.

Theoretical Information

A casting is a metal object produced by solidifying molten metal in a mold. The shape of the object is determined by the shape of the mold cavity. The casting process, also known as founding, involves melting metal and pouring it into the mold cavity, which is close to the final dimensions of the finished form. Many types of complex objects ranging in size from a few grams to thousands of kilograms are produced in a metal casting facility. Castings are produced by various casting processes such as sand, permanent mold, investment, and lost foam. While all metals can be cast, the most predominant are iron, steel, aluminum, copper, magnesium, and zinc-based alloys. Metal castings are used in more than 90% of all manufactured goods and find a wide range of applications in various sectors such as transportation (automotive, rail-way, naval, aerospace), mining, forestry, power generation, petrochemical, construction machinery, sporting goods, household appliances, and farm equipment.

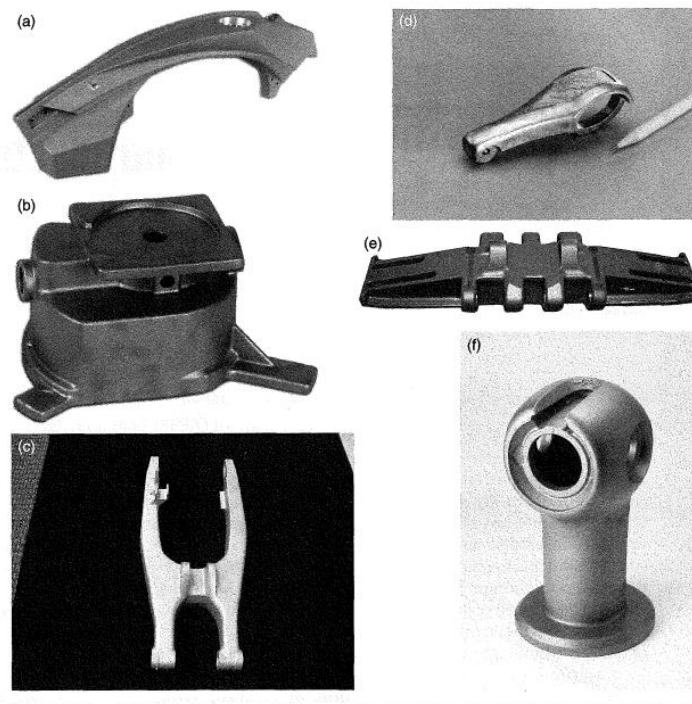


Figure 1 Typical castings in major alloys, (a) This motorcycle frame component was produced via the nobake sand casting process in 356 aluminum with T6 treatment temper, (b) The bronze alloy used for this dental suction pump was selected for its high strength, mechanical properties, and wear resistance, (c) Produced for a racing motorcycle, this one-piece magnesium casting replaced a three-piece aluminum part. The component is 33% lighter than the original, which impacts the overall performance of the bike, (d) This miniature zinc casket arm weighs less than 6 oz. (e) This NASA component for the space shuttle crawler transporter, produced with modified 4320 steel alloy via V-process casting, met reduced surface hardness requirements while maintaining high material strength, (f) This ductile iron green sand casting is the main structural element of the Spartan hydrant, enclosing and protecting its working parts.



2.1 Advantages of Casting Process

Certain advantages are inherent in the metal casting processes. These may form the basis for choosing casting as a process to be preferred over other shaping processes. Some of the reasons for the success of the casting process are as follows:

- The most intricate of shapes, both external and internal, may be cast. As a result, many other manufacturing operations such as machining, forging, and welding may be minimized or eliminated.
- Because of their metallurgical nature, some metals can only be cast to shape since they cannot be hot-worked into bars, rods, plates, or other shapes from ingot form as a preliminary to other processing. A good example of casting is the family of cast irons which are low cost, extremely useful, and exceed the total of other metals in tonnage cast.
- Casting is a simplified manufacturing process. An object cast as a single piece often would otherwise require multiple manufacturing steps (stamping and welding, for example) to be produced any other way.
- Casting can be a low-cost, high-volume production process, where large numbers of a given component may be produced rapidly. Typical examples are plumbing parts and automotive components such as engine blocks, manifolds, brake calipers, steering knuckles, and control arms.
- Extremely large, heavy metal objects such as pump housings, valves, and hydroelectric plant parts which could weigh up to 200 tons may be cast. These components would be difficult or economically impossible to produce otherwise.
- Some engineering properties such as machinability, bearing, and strength are obtained more favorably in cast metals. In addition, more uniform properties from a directional standpoint can be expected, which is not generally true for wrought products.
- Casting technology has progressed significantly, allowing products to be cast with very thin cross sections, often referred to as "thin-wall-casting"; such capabilities allow designers to reduce the casting weight that is often assumed necessary for production.
- One has to consider the economic advantages of the casting process. In the aerospace industry, some components are still being machined out of forged or rolled pieces despite the fact such pieces can be cast more eco-nomically to meet the design criteria, especially with respect to strength and toughness.

Table 1 World Production of Castings during 2009 to 2011 (in metric tons)

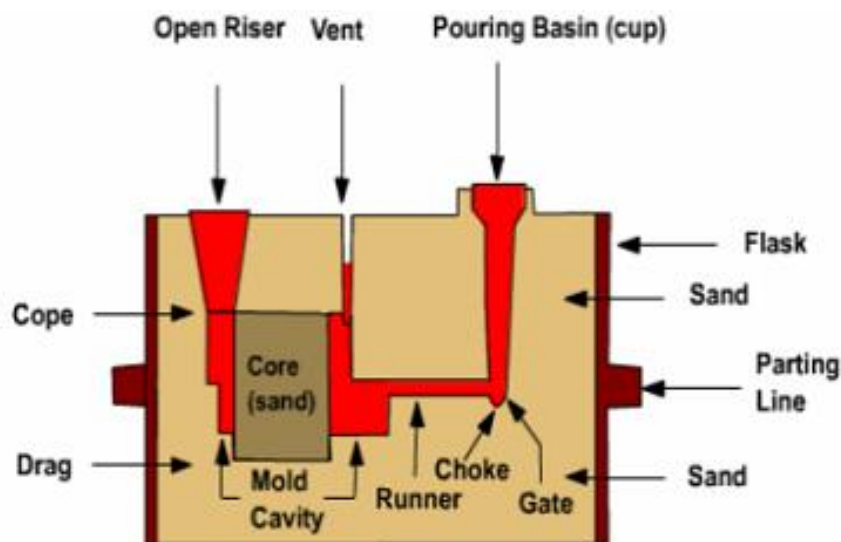
Metal	2009	2010	2011
Gray iron	37,749	43,258	45,870
Ductile iron	29,404	23,451	24,782
Malleable iron	1,013	-	-
Steel	9,070	10,215	10,342
Copper alloys	1,488	1,652	1,799
Aluminum alloys	9,477	10,879	11,319
Magnesium alloys	149	196	181
Zinc alloys	470	528	505
Total	80,895	91,673	98,593

Source: From Spada [3].

Note: Global forecast is for 102 million tons by 2015.

Casting Terms

- 1. Flask:** A metal or wood frame, without fixed top or bottom, in which the mold is formed. Depending upon the position of the flask in the molding structure, it is referred to by various names such as drag-lower molding flask, cope-upper molding flask, cheek-intermediate molding flask used in three piece molding.
- 2. Pattern:** It is the replica of the final object to be made. The mold cavity is made with the help of pattern.
- 3. Parting line:** This is the dividing line between the two molding flasks that makes up the mold.
- 4. Molding sand:** Sand, which binds strongly without losing its permeability to air or gases. It is a mixture of silica sand, clay, and moisture in appropriate proportions.
- 5. Facing sand:** The small amount of carbonaceous material sprinkled on the inner surface of the mold cavity to give a better surface finish to the castings.
- 6. Core:** A separate part of the mold, made of sand and generally baked, which is used to create openings and various shaped cavities in the castings.
- 7. Pouring basin:** A small funnel shaped cavity at the top of the mold into which the molten metal is poured.
- 8. Sprue:** The passage through which the molten metal, from the pouring basin, reaches the mold cavity. In many cases it controls the flow of metal into the mold.
- 9. Runner:** The channel through which the molten metal is carried from the sprue to the gate.
- 10. Gate:** A channel through which the molten metal enters the mold cavity.
- 11. Chaplets:** Chaplets are used to support the cores inside the mold cavity to take care of its own weight and overcome the metallostatic force.
- 12. Riser:** A column of molten metal placed in the mold to feed the castings as it shrinks and solidifies. Also known as "feed head".
- 13. Vent:** Small opening in the mold to facilitate escape of air and gases.



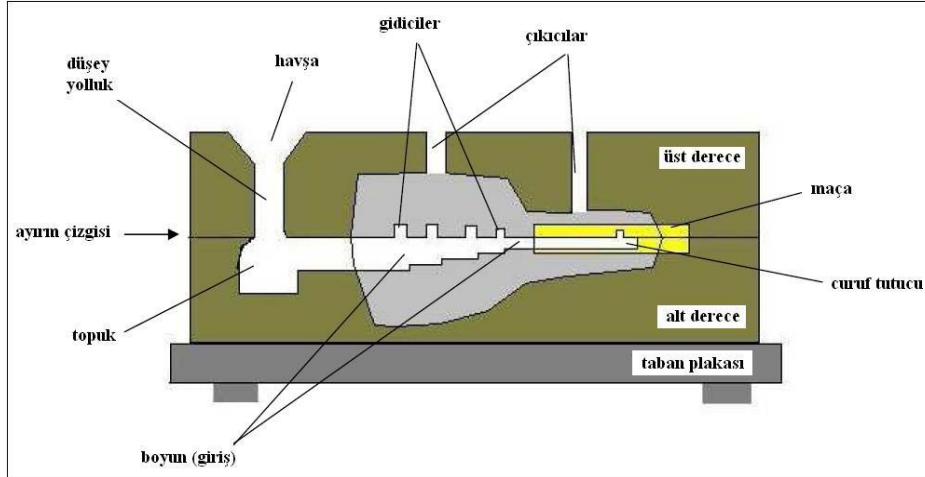


Figure 2 Mold section

Casting Process

Practically all the detailed operations that enter into the making of sand castings may be categorized as belonging to one of five fundamental steps of the process:

1. *Pattern making (including core boxes)*
2. *Core making*
3. *Molding*
4. *Melting and pouring*
5. *Cleaning*

Pattern making

Patterns are required to make molds. The mold is made by packing some readily formed plastic material, such as molding sand, around the pattern. When the pattern is withdrawn, its imprint provides the mold cavity, which is ultimately filled with metal to become the casting. Thus molding requires, first, that patterns to be made. A pattern, as shown in Figure 2, may be simply visualized as an approximate replica of the exterior of a casting. If the casting is to be hollow, as in the case of a pipe fitting, additional patterns, referred to as core boxes, are used to form the sand that is used to create these cavities.

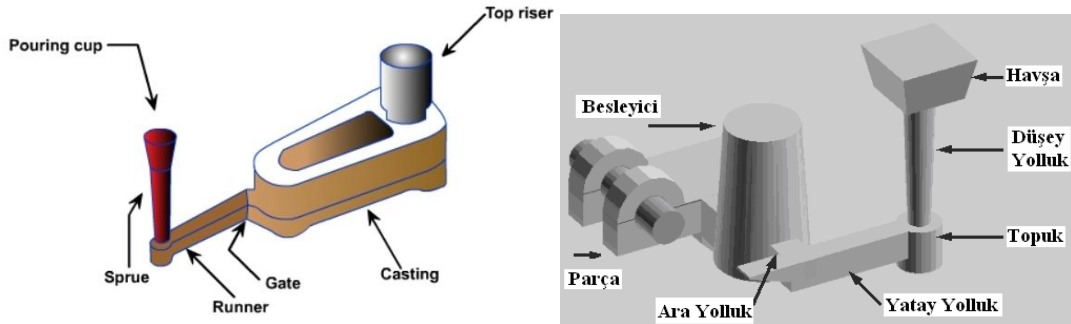


Figure 3 Pattern

Patterns may be constructed from the following materials. Each material has its own advantages, limitations, and field of application. Some materials used for making patterns are: wood, metals and alloys, plastic, plaster of Paris, plastic and rubbers, wax, and resins. To be suitable for use, the pattern material should be:

1. Easily worked, shaped and joined
2. Light in weight
3. Strong, hard and durable
4. Resistant to wear and abrasion
5. Resistant to corrosion, and to chemical reactions
6. Dimensionally stable and unaffected by variations in temperature and humidity
7. Available at low cost

The usual pattern materials are wood, metal, and plastics. The most commonly used pattern material is wood, since it is readily available and of low weight. Also, it can be easily shaped and is relatively cheap.

Core Making

Most simply defined, cores are sand shapes which form the contour of a casting that is not molded with a pattern. Forming internal cavities thus depends mainly on cores which can be inserted into a mold of the casting exterior. Through their use in forming complex internal cavities, cores provide the casting process its ability to make the most intricate of shapes, eliminate much machining, and in fact produce shapes which would be impossible to machine.

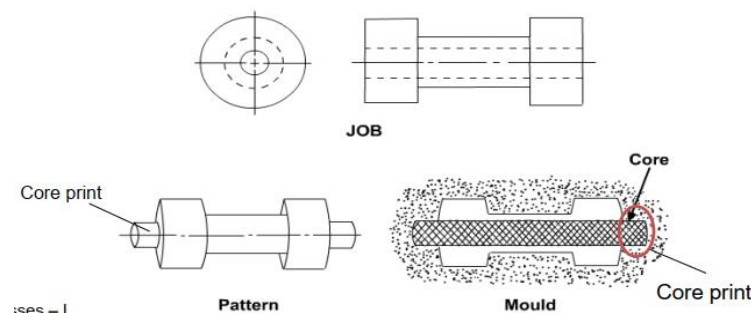


Figure 4 Core

Cores may be made of metal, plaster, and investment and ceramic materials, as well as core sand. To achieve the utmost of intricacy in castings, cores must be collapsible after the metal is poured. Metal ores, used in permanent-mold, or die casting, do not have collapsibility and therefore have shape limitations. However, sand cores and some other materials do not have this handicap and can therefore produce almost any desired degree of casting intricacy. Sand cores, along with sand molding, are the most frequently used.

Molding

Molding consists of all operations necessary to prepare a mold for receiving molten metal.

Sand Casting

Sand casting, the most widely used casting process, utilizes expendable sand molds to form complex metal parts that can be made of nearly any alloy. Because the sand mold must be destroyed in order to remove the part, called the casting, sand casting typically has a low production rate. The sand casting process involves

the use of a furnace, metal, pattern, and sand mold. The metal is melted in the furnace and then ladled and poured into the cavity of the sand mold, which is formed by the pattern. The sand mold separates along a parting line and the solidified casting can be removed. Sand casting is used to produce a wide variety of metal components with complex geometries. These parts can vary greatly in size and weight, ranging from a couple ounces to several tons. Some smaller sand cast parts include components as gears, pulleys, crankshafts, connecting rods, and propellers. Larger applications include housings for large equipment and heavy machine bases. Sand casting is also common in producing automobile components, such as engine blocks, engine manifolds, cylinder heads, and transmission cases.

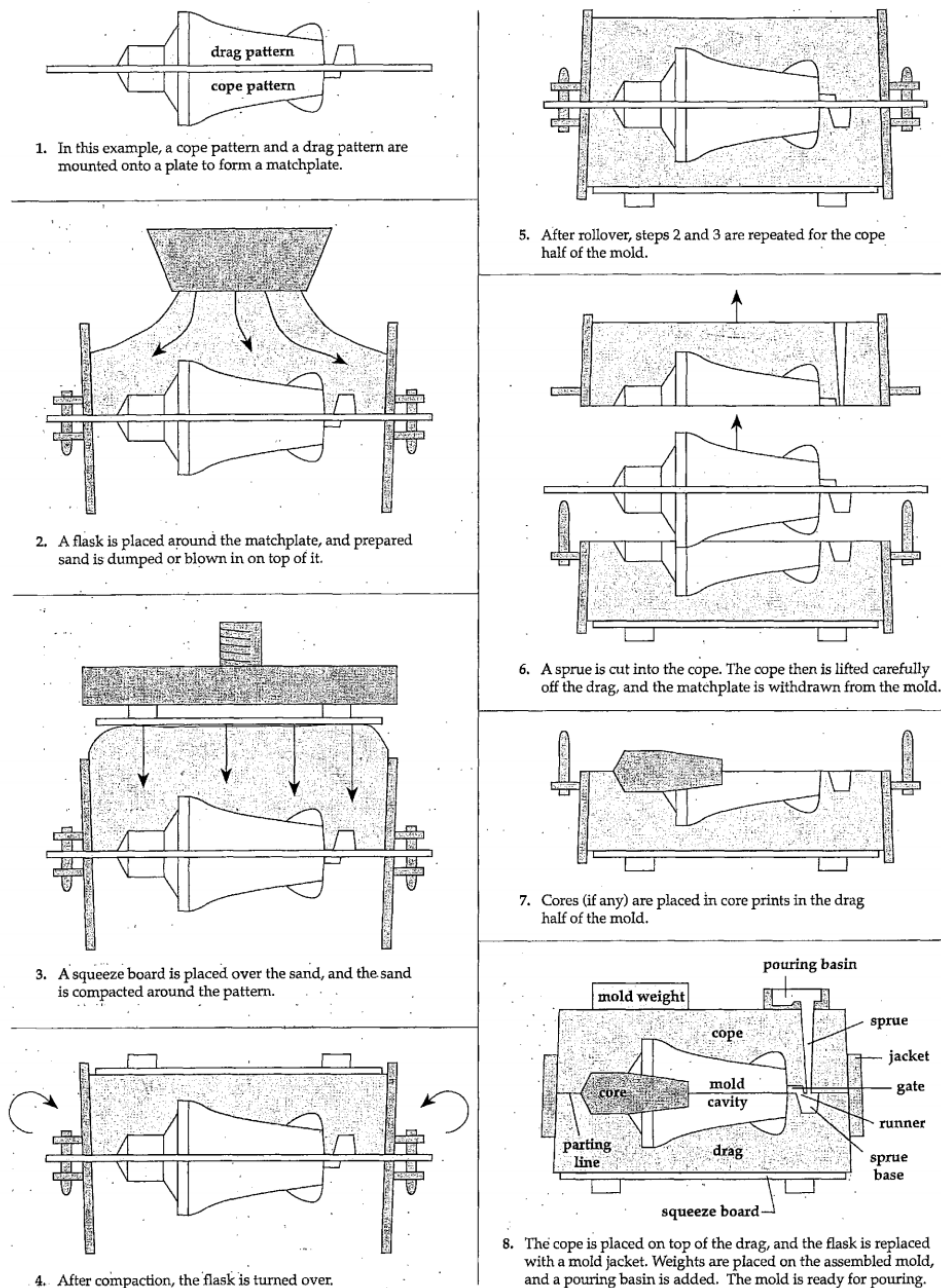


Figure 6 Steps of making sand mold



a) Molding Material and Properties

A large variety of molding materials is used in foundries for manufacturing molds and cores. They include molding sand, system sand or backing sand, facing sand, parting sand, and core sand. The choice of molding materials is based on their processing properties. The properties that are generally required in molding materials are:

Refractoriness: It is the ability of the molding material to resist the temperature of the liquid metal to be poured so that it does not get fused with the metal. The refractoriness of the silica sand is highest.

Permeability: During pouring and subsequent solidification of a casting, a large amount of gases and steam is generated. These gases are those that have been absorbed by the metal during melting, air absorbed from the atmosphere and the steam generated by the molding and core sand. If these gases are not allowed to escape from the mold, they would be trapped inside the casting and cause casting defects. To overcome this problem the molding material must be porous. Proper venting of the mold also helps in escaping the gases that are generated inside the mold cavity.

Green Strength: The molding sand that contains moisture is termed as green sand. The green sand particles must have the ability to cling to each other to impart sufficient strength to the mold. The green sand must have enough strength so that the constructed mold retains its shape.

Dry Strength: When the molten metal is poured in the mold, the sand around the mold cavity is quickly converted into dry sand as the moisture in the sand evaporates due to the heat of the molten metal. At this stage the molding sand must possess the sufficient strength to retain the exact shape of the mold cavity and at the same time it must be able to withstand the metallostatic pressure of the liquid material.

Hot Strength: As soon as the moisture is eliminated, the sand would reach at a high temperature when the metal in the mold is still in liquid state. The strength of the sand that is required to hold the shape of the cavity is called hot strength.

Collapsibility: The molding sand should also have collapsibility so that during the contraction of the solidified casting it does not provide any resistance, which may result in cracks in the castings. Besides these specific properties the molding material should be cheap, reusable and should have good thermal conductivity.

b) Molding Sand Composition

The main ingredients of any molding sand are; base sand, binder, and moisture.

Base Sand: Silica sand is most commonly used base sand. Other base sands that are also used for making mold are zircon sand, Chromite sand, and olivine sand. Silica sand is cheapest among all types of base sand and it is easily available.

Binder: Binders are of many types such as; clay binders, organic binders and inorganic binders. Clay binders are most commonly used binding agents mixed with the molding sands to provide the strength. The most popular clay types are kaolinite or fire clay ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and bentonite ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$). Bentonite can absorb more water which increases its bonding power.

Moisture: Clay acquires its bonding action only in the presence of the required amount of moisture. When water is added to clay, it penetrates the mixture and forms a microfilm, which coats the surface of each flake of the clay. The amount of water used should be properly controlled. This is because a part of the water,



which coats the surface of the clay flakes, helps in bonding, while the remainder helps in improving the plasticity. A typical composition of molding sand is given in Table 2.

Table 2 Composition of molding sand

Molding Sand Constituent	Weight Percent
Silica Sand	92
Clay	8
Water	4

c) Advantages and Disadvantages of Sand Molding

Advantages of sand molding are:

- 1) Suitable for casting iron and non-ferrous metal alloys.
- 2) Sand mold is a suitable method for both small and large parts.
- 3) Mold material is cheap and abundant.
- 4) Suitable for a small number of parts.
- 5) Molding cost is the lowest casting method.

Disadvantages of sand molding are:

- 1) Not suitable for mass production.
- 2) Surface and size accuracy is not good.
- 3) Very fine details are difficult to obtain.
- 4) The parts obtained from the casting are subjected to other processes.
- 5) Molding causes large time loss.
- 6) Material consumption is phase.

Melting

Melting is an equally important parameter for obtaining a quality castings. A number of furnaces can be used for melting the metal, to be used, to make a metal casting. The choice of furnace depends on the type of metal to be melted.

Cleaning

Cleaning refers to all operations necessary to the removal of sand, scab and excess metal from the casting. The casting is separated from the molding sand and transported to the cleaning department. Burned sand and scale are removed to improve the surface appearance of the casting. Excess metal, in the form of fins, wires, parting-line fins, and gates, is cut off. Defective castings may be salvaged by welding or other repair. Inspection of the casting for defects and general quality follows. The casting is then ready for shipment or further processing for example, heat-treatment, surface treatment, or machining.



Experimental Procedure

Mold Making

- A specified amount of sand, bentonite and water are loaded into the large sand mixer.
- It is mixed until it becomes suitable for molding.
- Top and bottom are placed on top of the molding plate.
- The pattern is placed between two flasks.
- Graphite is sprinkled on the pattern.
- Flask is filled with sand.
- Gradually compact the sand with hand tools and air hammer.
- Cope and drag are separated and pattern extracted.
- If necessary, the mold is repaired.
- The cope and drag are reassembled and ready for casting.

Casting

- The prepared mold is brought to the front of the melting furnace.
- Sand is poured around the mold and weights are placed on it.
- The crucible is removed from the furnace and slag skimmed.
- The liquid metal is poured into the mold.
- The mold is broken to remove the casting.

References

- [1] Sahoo M, Sahu S, "*Principles of Metal Casting*", Third Edition, McGraw-Hill Education, Printed in the United States of America, 2014.
- [2] Jorstad JL, Rasmussen WM, "*Aluminum Casting Technology*", Second Edition, AFS.
- [3] Cigdem M, Casting Technology lecture notes.



3. METALLOGRAPHY EXPERIMENT

OBJECTIVE:

1. To learn and to gain experience in the preparation of metallographic specimens.
2. To examine and analyze the microstructures of metals and metallic alloys.

MATERIALS AND EQUIPMENT:

Grinders, polishing wheels, drying fans, and metallurgical microscopes. Acrylic resin etching solutions (nitric acid, alcohol), Al_2O_3 (5 μ m, 1 μ m and 0.05 μ m) and consumable supplies as needed and given engineering alloy specimens.

THEORETICAL BACKGROUND:

Metallography is essentially the study of the structural characteristics or constitution of a metal or an alloy in relation to its physical and mechanical properties. The most important part of metallography deals with the microscopic examination of a prepared metal specimen. Correct preparation begins with the selection of a suitable specimen and continues to the etching stage where the structure of the specimen is revealed. The microscopic examination then defines clearly such structural characteristics as grain size, the size, shape and distribution of secondary phases and non-metallic inclusions; and segregation and other heterogeneous conditions.

These characteristics profoundly influence the mechanical properties and physical behavior of the metal. Metallographic examination can provide quantitative information about specimen grain sizes, amount of interfacial area per unit volume, and the amount and distribution of phases. When these and other constitutional features are determined by microscopic examination and the extent to which they exist in the microstructure is known, it is then possible to predict with considerable accuracy the expected behavior of the metal when used for a specific purpose. Of equal importance is the fact that, within limits, the microstructure can provide an accurate picture of the mechanical and thermal treatments that a metal has received.

Preparation of Specimens

The technique for preparing metal sections can be divided into two groups, those processes involving the use of emery papers and coarse abrasives (grinding) and the subsequent operations using fine abrasives (polishing treatments). Grinding must be carried out carefully in such a way that all microscopic constituents in the surface are preserved and that the grinding medium is not embedded in the sample. To achieve this, the specimen is ground on successively finer grades of emery (sand) paper. During grinding, the specimen is held with the newly formed scratches at right angles to the scratches introduced on the preceding paper. Undue pressure should be avoided since the disturbed layer this produces on the surface can extend to considerable depth. For some heat treated alloys and in particular for many of the soft metals, it is an advantage to use paper thoroughly wetted. Grinding also removes surface deformations. After grinding, the specimen is washed thoroughly in water and then polished. Mechanical polishing can best be carried out by holding the specimen against a rotating disc covered with a suitable pad that is impregnated with either a suspension of polishing alumina in water or diamond dust oil.

Mounting of Specimens

It is frequently convenient to mount small specimens in bakelite or acrylic to aid specimen preparation,

grinding, polishing and etching. The basic idea is that bakelite powder is thermosetting. Therefore the specimen is placed in a tube 2/3 filled with powder. The tube is heated while the powder is compressed. The pressure and heat are removed when the powder has completely melted and the bakelite has set. To maintain orientation small shot are sometimes placed next to the specimen in some identifying arrangement.



Fig. 1: A Hot Mounting Press

Although inferior in quality to compression-type molding, cold molding (room temperature) is often used with epoxy to mount samples by simply mixing the epoxy and pouring it over a sample that is positioned facedown in a cold-mounting ring. When the epoxy cures the specimen can be prepared. Caution must be exercised when cold mounting due to relatively poor adhesion between the specimen edges and the epoxy plug; gaps often form which can degrade the quality of the specimen.



Fig. 2: Various resins used for cold mounting

Grinding and Polishing Procedure

The following instructions indicate the general method to be used in specimen preparation. The edges of cylindrical metal specimens must first be beveled off to avoid damaging the polishing cloths. For Mg and Al and their alloys, use the aluminum polishing wheels.

<u>Stage</u>	<u>Abrasive</u>	<u>Lubricant</u>	<u>Cloth</u>
Rough Grinding	Silicon Carbide	Tap Water	
Fine Grinding	Grit 240		
	Grit 320		
	Grit 400		
	Grit 600		
Rough Polishing	Gamma Alumina 1.0 μ	Tap Water	Rayon
Final Polishing	Gamma Alumina 0.05 μ	Tap Water	Rayon



Fig. 3: An Automatic Polishing Machine with Two Rotating Discs

It is important that abrasive is not carried from one part of a sequence to another. Therefore, you must wash both the specimens and your hands between each step. When grinding the specimens, they are rubbed forward in one direction until the surface is completely ground, that is, until only grinding marks due to the particular paper can be seen on the whole surface. For soft metals, further grinding for a short time is advisable after this condition is reached to remove any sub-surface deformation produced in previous operations. The direction of grinding is changed from paper to paper so that the removal of previous grinding marks is easily observed. Polishing is carried out on cloth covered rotating wheels. During the polishing, the specimen should be held firmly in contact with the polishing wheel, undue pressure should be avoided. During polishing, the specimen should be rotated or moved around the wheel to give an even polish. The specimens must be washed and dried before both polishing steps.

Etching

Etching is done to bring out the structure of the polished specimen. It is usually performed by subjecting the polished surface to the chemical action of an appropriate reagent. However, the polished specimen should first be examined unetched. Inclusions, flaws, scratches and other defects can be observed in this way, and if they are identified before etching, subsequent confusion and misinterpretation can be largely avoided. The specimen to be etched is treated by immersion in, or by swabbing with, the appropriate reagent. It is impossible to lay down general rules for the time of etching. Usually the desired effect will be produced between ten seconds and two minutes. The specimen after etching should be washed in a stream of running

water. The surface should be dried untouched by holding in air current. When selecting etching times, it is more desirable to under-etch than to over-etch. If a specimen, after a first attempt is found to be insufficiently etched, the etching process can usually be repeated without further preparation of the surface. A specimen that is over-etched can only be corrected by repolishing and then reetching for a shorter time.

Nital, a Nitric Acid - Alcohol mixture, is the etchant commonly utilized with common irons and steels. Nital is dripped onto the specimen using an eye-dropper or cotton swab. Ten seconds to one minute is usually sufficient for proper etching depending on sample and nital concentration. The sample is immediately washed under running water, rinsed with alcohol and dried in an air blast. Do not touch, wipe or swab the specimen following etching; dry off the rinsing alcohol on the specimen with the air blast and then move on to the microscopic examination stage!

Table 1: Etchants used for different materials

Materials	Composition	Application Procedure
Iron & Steel	1-5 Parts Nitric Acid 100 Parts Alcohol	Immerse/Swab
Copper & Brass	1 Part Ammonium Hydroxide 1 Part 3% Hydrogen Peroxide 1 Part Water	Swab
	5 g Ferric Chloride, 10 ml Hydrochloric Acid 100 ml Water	Immerse
Aluminum	5-10 g Ammonium Persulphate 1 ml Hydrofluoric Acid 99 ml Water	Immerse
	10 g Sodium Hydroxide, 100 ml Water	Immerse
Stainless Steels	10 g Oxalic Acid 100 ml Water	Use Electrolytically
	5 ml Sulfuric Acid 100 ml Water	Use Electrolytically

Microscopic Examination

Initial microscopic viewing should be done utilizing a stereo microscope, which reveals a three-dimensional scanning of the specimen surface. The specimen is placed on the stage of the microscope so that its surface is perpendicular to the optical axis.



Fig. 4: Stereo Microscope

Detailed viewing is done with a Metallurgical Microscope. A metallurgical microscope has a system of lenses (objectives and eyepiece) so that different magnifications (25X to 1000X) can be achieved. The important characteristics of the microscope are: (1) magnification, (2) resolution and (3) flatness of field. The resultant magnification is the product of the magnifying power of the objective and that of the ocular. Scanning Electron Microscopes (SEMs) are capable of magnifications up to 20,000X and Transmission Electron Microscopes (TEMs) are utilized to view at magnifications up to 100,000X for highly detailed microstructural study.



Fig. 5: Metallurgical Microscope

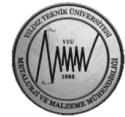
The Metallurgical Microscope

A metallurgical microscope differs from a biological microscope in the manner by which the specimen is illuminated. Because of the inability of visible radiation to propagate through a metal specimen, observations are made using light reflected from the polished surface. A horizontal beam of light is deflected by a plane glass reflector, upward and through a microscope objective onto the surface of the specimen. A certain amount of incident light will be reflected from the specimen surface back through the objective lens system and then through a second lens system, the microscope eyepiece.

The total visual magnification obtained by the combination of a given eyepiece and objective is equal to the product of the magnifications of the two systems. These magnifications are usually marked clearly on the appropriate parts. When examining a metallographic specimen, the objective of lowest magnifying power should first be used. Subsequently, greater detail of particular areas can be obtained by using progressively higher magnifications. The different objectives are mounted on a rotating head, so that their focal planes are very nearly at the same level. After focusing at the lowest magnification, only small adjustments should be necessary at higher magnifications.

Grain Size Determination

In single phase specimens, the ASTM grain size of the metal can be estimated by comparing the image at 100X with standard microstructure examples corresponding to standard grain sizes from 1 to 10. Also, suitable eyepieces etched with a square 0.01" x 0.01" in size can be used to calculate the number of grains per square inch, N.



The ASTM grain size number, n , can be calculated using the following relationship:

$$N (M/100)^2 = 2^{(n - 1)}$$

N = number of grains per square inch at 100X

n = ASTM grain size number

M = Magnification

For single phase materials, ASTM grain size number is given to denote the grain sizes. These are not the actual grain size values, but the latter can be derived from the ASTM grain size number, n ; the larger the grain size number, the smaller the grains. If there are **N** grains per square inch at a magnification M then there are $(N)^{1/2}$ grains along a 1 inch length. The size of each grain at magnification M is then $1/(N)^{1/2}$ inches.

The actual size of the grain is given by Actual **Grain Size** = $1/(N M)^{1/2}$

EXPERIMENTAL STUDY:

Please be careful while using the equipment in the lab. Switch off all equipment and tidy the lab before you leave.

Using steel, aluminum and/or brass (60% Cu; 40% Zn) specimen, and the metallurgical microscope, analyze the microstructure of your given engineering alloys. Identify the phase or phases present and the grain size of the material from your metallographic examination. Study the microstructures using the metallurgical microscope and appropriate phase diagrams. Provide interpretation of your microstructures and prepare a laboratory report of your experiment.

Stage I: Making Specimen Mounts:

Cold mounting procedure will be used to mount the specimens. Place the sample in a mounting cup with the help of mounting clips and then pour a mixture of resin mixture of two components). Now allow the resin to solidify (curing) and then take the sample out of the mounting cup. Applying release agent to the walls of the mounting cup before pouring the resin will help in easily removing the sample after curing process.

Stage II: Grinding

The specimens will be taken and grinded on different emery papers (SiC) using grinding machine.

Procedure:

- (1) Open water line located behind grinder.
- (2) Starting on the 120 and then 240 grit size, place prepared specimen, or metal face down of abrasive surface, and being sliding specimen against abrasive in a forward and backward motion.
- (3) Next, turn specimen 90 degrees and repeat above procedure on the 320 Grit surface.
- (4) Again turn specimen 90 degrees and repeat procedure (2) now on the 400 Grit surface.
- (5) Finally, turning specimen 90 degrees and repeat procedure (2) now on the 600 Grit surface.
- (6) Close water line.



Stage III: Polishing Wheels

Polish the specimen on polishing wheels using liquid suspension of Al_2O_3 and water, which is a very fine abrasive, until a mirror like finish is obtained. Start with $5\mu\text{m}$ and then with $1\mu\text{m}$ and then proceed to $0.05\mu\text{m}$ grit size Al_2O_3 powder polishing station. At this stage the microscopic examination may reveal cracks, seams, non-metallic inclusions, and any other similar scale inhomogeneities.

Stage IV: Etching the Surface

Etching is the selective attack by a chemical reagent that reveals the microstructural detail of the polished mount. The grain boundaries are attacked to a higher extent than grains because of their high energy. This results in depression of grain boundaries. To reveal the crystalline structure of the specimen, the polished surface is etched using appropriate etching solution. For this experiment use 3% Nital (97% Alcohol-3% Nitric Acid) to etch the surface of the polished steel specimen. For brass specimens 50% nitric acid solution can be used. The etching solution may be applied on the specimen using a swab. It is very important to not over etch or underetch the specimen.

Stage V: Microscopy

The etched specimen will be examined using metallurgical microscope. The digital image of the grain structure will be saved for further image analysis.

REFERENCES

- ASM Handbook, Metallography and Techniques
- Material Science and Engineering- An introduction by W. D. Callister
- Engineering Metallurgy- Part I by R. A. Higgins
- Materials Science and Eng. By V. Raghavan
- Manufacturing Engineering and Technology by S. Kalpakji



4. CORROSION EXPERIMENT

PART 4.1: CORROSION OF ZINC IN ACIDIC SOLUTION

4.1.1 AIM: Investigation of electrochemical behavior of zinc in acidic solution and calculation of corrosion rate by two different methods.

4.1.2 THEORIC INFORMATION

Corrosion is the occurrence of undesirable changes in the physical, chemical and mechanical properties of materials in general, metals and alloys in particular, due to the effect of the environment they are in. The main cause of corrosion is the desire of metals to return to their natural state. Electrochemical corrosion, a type of 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.

The desire of a metal to become an ion determines its activity and shows the tendency of the metal to undergo corrosion. EMF (Electromotive force) series, which show the standard electrode potentials of metals, are thermodynamic series obtained by calculation and give an idea about the activity of metals. In addition, galvanic series created by experiments in sea water can be more useful in comparing the activities of different metals and alloys.

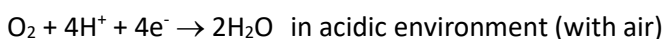
When different metals and alloys come into contact with each other in the same environment, the more active one is corroded by acting as an anode, while the other metal is protected from corrosion by acting as a cathode. On the other hand, two different metals do not necessarily have to be present in the environment for electrochemical corrosion to occur. Corrosion can also occur when a metal is alone in the electrolyte. Due to the different regions in the structure or surface of the metal, some parts of the metal can act as anodes and some parts as cathodes.

For electrochemical corrosion to occur, five elements must be present in the system. These are; 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 and the amount of dissolved oxygen in the electrolyte. The reactions taking place at the metal-electrolyte interface are given below:

On anode:



On cathode:



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.



The corrosion rate is practically defined as the mass of metal that moves away from a unit surface area per unit time. Various methods are available for the measurement of corrosion rate. Of these, the weight loss method and the Tafel extrapolation and linear polarization methods, which are performed by drawing polarization curves, are the most preferred methods. In addition, the fact that the cathodic reactions in electrochemical corrosion events are hydrogen or oxygen reduction allows, in some cases, to determine the rate of corrosion by determining the amount of gas released during the test. In determining the corrosion rate, the method that will give the most accurate result should be selected.

The corrosion rate can be expressed in various units. The most commonly used ones are; mg/dm².day (mdd), mm/year, ipy (inch per year) and mpy (mile per year). These units are interchangeable (eg: 1 ipy = 1000 mpy = 25.4 mm/year).

When the weight loss in the test sample is determined, it is possible to calculate the corrosion rate with the help of the following formula.

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

H: corrosion rate

K: constant for the desired corrosion rate unit (3.45x10⁶ for 'mpy')

G: weight loss (g)

A: surface area exposed to the solution (cm²)

d: metal density (g/cm³)

t: duration of experiment (s)

The units of the variables in this formula and the value of the constant number 'K' vary according to the corrosion rate unit to be calculated. In this experiment, the corrosion rate will be calculated in 'mpy'.

4.1.3 EXPERIMENTAL PROCEDURES

Equipment and Materials: Zinc, beaker, glass funnel, 0.1 M HCl solution, burette, pipette pump, drying machine, scales, polishing papers.

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.

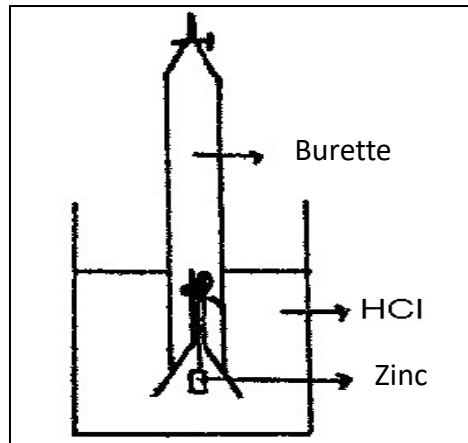


Figure 3.1 Experimental set-up

4.1.4 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 (mg) -duration (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 4.2: CORROSION OF LEAD IN ACIDIC SOLUTION

4.2.1 AIM: Measuring the corrosion rate of lead in acidic solution by Tafel Extrapolation Method

4.2.2 THEORIC INFORMATION:

In a corroded electrode, a cathodic reaction takes place simultaneously with the anodic reaction of the metal, depending on the environment. Thus, a mixed potential called 'corrosion potential (E_{corr})' is formed on the electrode surface as a result of the balance of two different reactions, one anodic and the other cathodic.

If an external current is applied to the electrode, the electrode potential takes on a value different from that at which no current is flowing. The change in electrode potential when current is applied is called 'polarization'. Experimentally obtained polarization curves can be used to determine the velocity of the metal in the electrolyte in question. For this purpose, two electrochemical methods are applied.

- 1- Tafel extrapolation method
- 2- Linear polarization method

Tafel extrapolation method:

Polarization (or current-potential) curves are curves plotted on a semi-logarithmic scale. After the applied external current reaches a certain value, there is a significant break in these curves and after this point the logarithm of the applied external current ($E - \log i$) shows a linear change. This region where the logarithm of the current changes linearly is called the 'Tafel Region'.

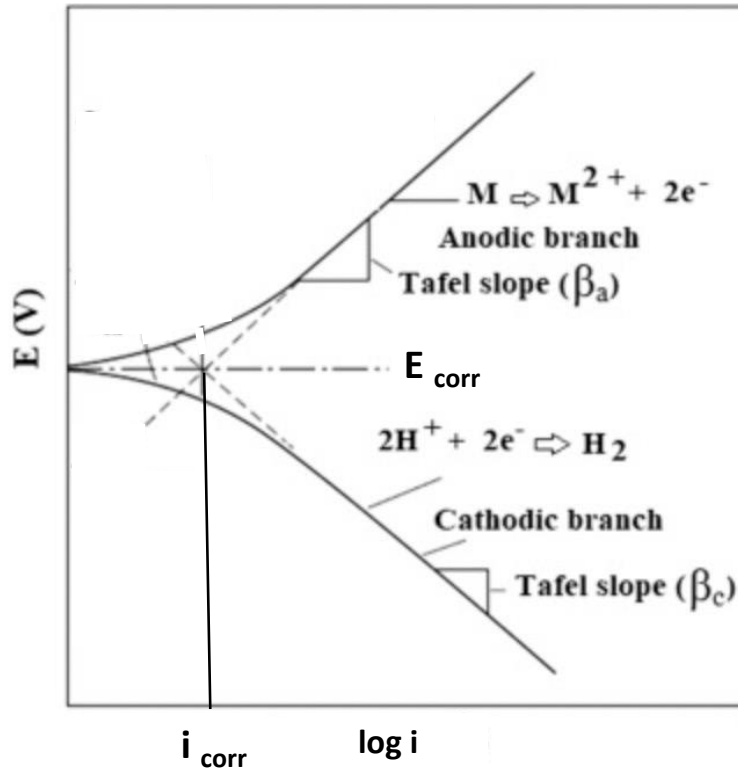


Figure 4.2. Tafel region of the polarization curve

If the lines in the Tafel region are extrapolated to the corrosion potential, the cutoff gives the 'corrosion current density (i_{corr})' value. By substituting the corrosion current density value in the formula below, the corrosion rate is calculated in mm/year.

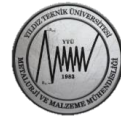
$$\text{Corrosion rate} = K \times (i_{corr} \times EW) / d$$

K = constant number, 3.27×10^{-3} mm.g/ μ A.cm.year,

i_{corr} = current density (A/cm²),

EW = equivalent weight of the sample,

d = density of the sample, g/cm³



4.2.3 EXPERIMENTAL PROCEDURES

Equipment and Materials: Potentiostat, lead sample, 1 M H₂SO₄ solution, 5-necked cell, lead counter electrodes, saturated calomel reference electrode, crocodile cable, dryer machine, glue gun, silicone.

Experimental:

Lead sample is washed and dried to remove dust and dirt on its surface. It is bonded with crocodile cable and covered with silicone except an active surface area of 1 cm². 1 M H₂SO₄ solution is filled into the 5-necked cell. Saturated calomel electrode as reference electrode, lead electrodes as counter electrode and lead sample as working electrode are placed in the cell. With the help of a potentiostat, first, the open circuit potential (OCP) value of the system is measured. Then, the sample is scanned within the determined potential range, including the OCP value, to obtain a semi-logarithmic current-potential curve. The i_{cor} value obtained from this curve is substituted in the formula given above and the corrosion rate is calculated in mm/year.

4.2.4 REQUIREMENTS:

1. Write the anodic and cathodic reactions that took place in the experiment for the lead sample in H₂SO₄ solution.
2. Calculate the corrosion rate of the sample in mm/year with the help of the i_{cor} value obtained from the Tafel curve.
3. Convert the corrosion rate calculated in mm/year for lead into mpy and compare it with the corrosion rate calculated in mpy for the zinc sample.

4.2.5 REFERENCES:

H. Yalçın, M. Gürü, "Elektrokimya ve Uygulamaları", Palme Yayıncılık, Ankara, 2010.



5. POWDER METALLURGY EXPERIMENT

Purpose of Powder Metallurgy: Metal and metal alloys are melted into a durable body with the help of pressure and temperature without melting their dust. 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 (Dust particles into a single part with various operations),
3. Sintering and final parts production with secondary operations if necessary

NAME OF THE EXPERIMENT: Apparent Density (wet Density)

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

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

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 $2,80\text{-}3,20 \text{ g} / \text{cm}^3$. This value can be up to $5 \text{ g} / \text{cm}^3$ for dusts produced by gas atomization. This value varies between $2,80\text{-}3,00 \text{ g} / \text{cm}^3$ for copper powders and $3,00\text{-}3,25 \text{ g} / \text{cm}^3$ 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.

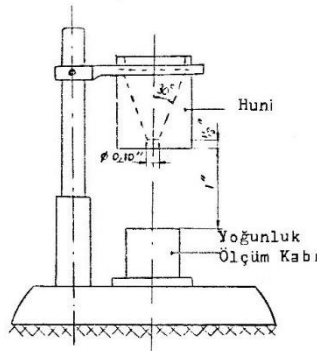


figure 1. Measurement of Masonry Density.

NAME OF THE EXPERIMENT: Fluidity test

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

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

THEORETICAL KNOWLEDGE AND EXPERIMENT

The purpose of this test is to determine the fluency values of raw materials from X. 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.

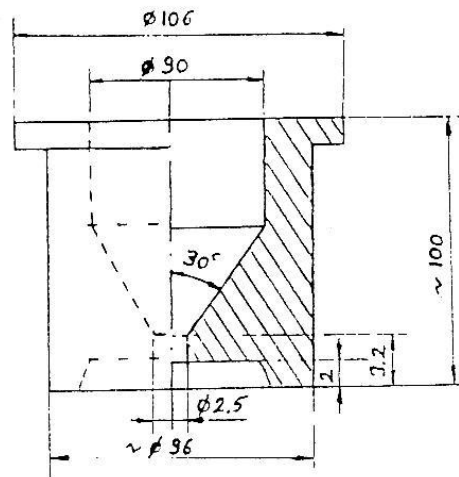


figure2. An Experimental Funnel for Determining Fluency is Shown Schematically.

NAME OF THE EXPERIMENT: compressibility (Green Density)

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

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

THEORETICAL KNOWLEDGE AND EXPERIMENT

: This property corresponds to the density obtained when the powder is under pressure. 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 pressability 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% Gives theoretical density.

%84,5 Filled 15.5% Pore

NAME OF THE EXPERIMENT: Sieve Analysis, Dimensional Distribution and Calculation of Average Particle Size

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

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

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 (from the big eyes) 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. How to try the sieve with the number of sieves and sieve is specified in the standards. The screens must be anti-magnetic.

chart 1. Sieve Analysis Chart (example

Elek göz açıklığı d (µm)	Elek üstü ΔR (% hacim)	Toplam elek üstü miktarı R (%)	Toplam elek altı miktarı D(%)	Her göz için ortalama tane boyutu 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: $d_o = \sum \Delta R * d_a / 100$

d_o : Arithmetic mean grain diameter

%R: Quantity on each sieve,%

R: Sum of sieve size,%

d_a : average grain size for each sieve, mm

D: Amount passed through the screen,%

example:

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

NAME OF THE EXPERIMENT: **compressing**

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

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

THEORETICAL KNOWLEDGE AND EXPERIMENT

Densification in Powder Metallurgy is the second important process. Pressing; prepared metal powder mixture to reach the predetermined density of the press and staples in the appropriate press is to be compressed. 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

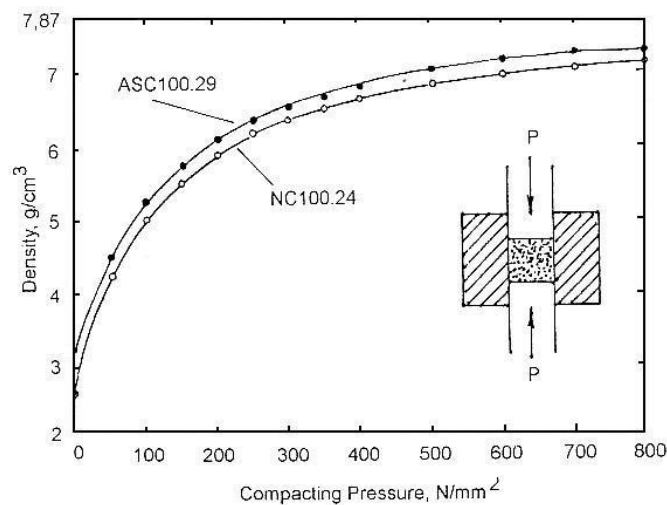


figure 4. Density-pressure relationship for two commercial iron powders

- * pressure \uparrow , density \uparrow , pore \downarrow
- * pore \uparrow , density \downarrow
- * pore \uparrow , strength \downarrow
- * pore \uparrow , lubricant ability \uparrow

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)

NAME OF THE EXPERIMENT: Sintering Processes Applied to Metal Powders

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

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

THEORETICAL KNOWLEDGE AND EXPERIMENT

Sintering; Pressed powder is heat treatment without disrupting the shape of the 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.

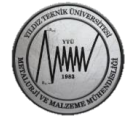
Sintering temperature and time; sintering the sintering temperature and duration of a sintering according to the desired properties should be determined. The main reason for the low density and strength in the parts is the very low sintering temperature and time. The sintering temperature should be as close as possible to the melting temperature of the powder.

chart.2 : Sintering temperature and time of some metals and alloys

powder materials	Sintering temperaturee (°C)	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

RESOURCES

- Toz Metalürjisi Ders Notları, Adem BAKKALOĞLU, 2015.
- Toz Metalürjisi ve Parçacıklı Malzeme İşlemleri, Randall M. GERMAN, 2007
- Höganäs Handbook For Sintered Components, 1997.
- Powder Metallurgy Science, Randall M. GERMAN, 1994.
- ASM Handbook Volume 7, Powder Metallurgy, 1993.



6. HYDROMETALLURGY EXPERIMENT

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.

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.

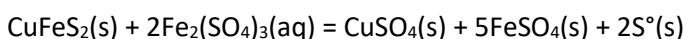
Ores can be subject to some preparation treatments between furnace productions and leach process. Pretreatments before the leaching are crushing, grinding, beneficiation and roasting.

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.

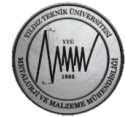
Copper ores usually are processed by pyrometallurgical routes for a long time. However pyrometallurgical techniques are recently replaced with hydrometallurgical ones. Sulphur dioxide (SO₂) emission, requirement of ore beneficiation, loss of other metals and high costs are disadvantages of pyrometallurgical 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.



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:

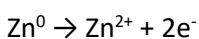
1. Grain size of the ore,
2. Composition of the ore,
3. Composition and concentration of the solvent,
4. Contact time of the ore with the solvent,
5. Leaching temperature

Cementation

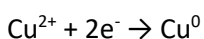
Any metal in the solution dissolves another metal (granule, plate, powder, scrap) that has a more negative electrode potential than it in the EMF series of metals is called "cementation". The cementation process is applied either to the production of a metal or to the removal of impurities from the electrolyte.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

Reactions occurring in copper cementation process:

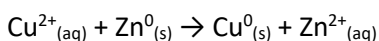
1. Formation of Zn^{2+} ions by anodic half-cell reaction:



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



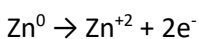
3. Total cell reaction:



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

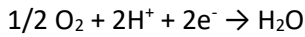
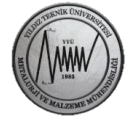
$2H^+ + 2e^- \rightarrow H_2$ the secondary reaction evolving according to the reaction is activated. Thus, there is unnecessary increase of cementator consumption. When cementation is being done, the solutions are either not mixed or very slowly mixed that not allowed to aeration. In case of excessive 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:



Cathodic reaction:





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.



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

In this equation,

E = Real potential (V)

E⁰ = 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;

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

$$E^0_{Cu} + (RT/nF) \times \ln(a_{Cu^{2+}}) = E^0_{Fe} + (RT/nF) \times \ln(a_{Fe^{2+}}) \quad (4)$$

$$0.34 + (0.059/2) \times \log(C_{Cu^{2+}}) = -0.444 + (0.059/2) \log(C_{Fe^{2+}}) \quad (5)$$

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

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

This result theoretically means that there is only 1 copper ion (Cu²⁺) per 10²⁷ iron ions (Fe²⁺) 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.



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

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



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:

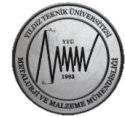
% Cementation efficiency % = [amount of precipitated copper (g / l) / amount of copper in solution (g / l)] x 100.

5. ASSIGNMETNS 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.

6. REFERENCES

2. Aydoğan, S. (2000), "Hafif Madentepe Bakır Cürüflarının Sülfürik Asit, Asidik Ferik Sülfat ve Amonyak Liçi Koşullarının Belirlenmesi", Doktora Tezi, Cumhuriyet Üniversitesi Fen Bilimleri Enstitüsü.
3. Canbazoğlu, M. (1979), "Hidrometalurjide Yeni Gelişmeler", TMMOB Maden Müh Odası, Madencilik, sayfa 21-38.
4. Canbazoğlu, M. (1979), "Sülfürlü Cevherlerin Hidrometalurjik Yöntemlerle Değerlendirilmesi", TMMOB Maden Müh.Odası, Madencilik Dergisi, sayfa 9-20.
5. Canbazoğlu, M. (1986), "Hidrometalurji", TMMOB Maden Müh. Odası, Madencilik Dergisi, sayfa 39-52.
6. Venkatachalam, S (1991), "Treatment of Chalcopyrite Concentrates by Hydrometallurgical Techniques", Mineral Engineering, 4(7-11), 1115-1126.
7. Bor, F.Y., 1989, "Ekstraktif Metalurji Prensipleri Kısım:II", İTÜ Matbaası, İstanbul.
8. Habashi, F., Principle of Extractive Metallurgy, Volume 2, Science Publishers, Paris, 1980.



7. HEAT TREATMENT EXPERIMENT

Objective:

1. Distinguish between hardness and hardenability.
2. Understand the concept of mass effect and ruling section.
3. Perform Jominy test as a method to indicate hardenability.

Theoretical Knowledge:

Hardenability is the ability of an alloy to be hardened by the formation of martensite as a result of a given heat treatment. It is a qualitative measure of the rate at which hardness drops off with distance into the interior of a specimen as a result of diminished martensite content. With the Jominy end-quench test, except for alloy composition, a cylindrical specimen is austenitized and upon removal from the furnace, the lower end is quenched by a jet of water. The cooling rate is a maximum at the quenched end and diminishes with position from this point along the length of the specimen. With diminishing cooling rate more time is allowed for carbon diffusion and the formation of a greater portion of the softer pearlite or bainite. A steel alloy that is highly hardenable will retain large hardness values for relatively long distances. The presence of nickel, chromium, and molybdenum in the alloy steels delay the austenite-to-pearlite and/or bainite reactions, thus permitting more martensite to form for a particular cooling rate.

Factors Affecting Hardenability:

- Carbon Content
- Alloying elements
- Grain size
- Cooling rates

TTT diagrams for (a) hypoeutectoid, (b) eutectoid and (c) hypereutectoid steels are given in Fig. 1.

As the carbon percentage increases A_3 decreases, similar is the case for A_r3 , i.e. austenite stabilises. So the incubation period for the austenite to pearlite increases i.e. the C curve moves to right. However after 0,8 wt% C any increase in C, A_{cm} line goes up, i.e. austenite become less stable with respect to cementite precipitation. So transformation to pearlite becomes faster. Therefore C curve moves towards left after 0,8% C.

Almost all alloying elements (except, Al, Co) increases the stability of supercooled austenite and retard both proeutectoid and the pearlitic reaction and then shift TTT curves of start to finish to right or higher timing. This is due to i) low rate of diffusion of alloying elements in austenite as they are substitutional elements, ii) reduced rate of diffusion of carbon as carbide forming elements strongly hold them.

However Al, and Co increase rate of nucleation and growth of both ferrite or pearlite and therefore shift TTT diagram to left. In addition under the complex diffusional effect of various alloying element the simple C shape behaviour of TTT diagram get modified and various regions of transformation get clearly separated. There are separate pearlitic C curves, ferritic and bainitic C curves and shape of each of them are distinct and different.

Fine grain size shifts S curve towards left side because it helps for nucleation of ferrite, cementite and bainite.

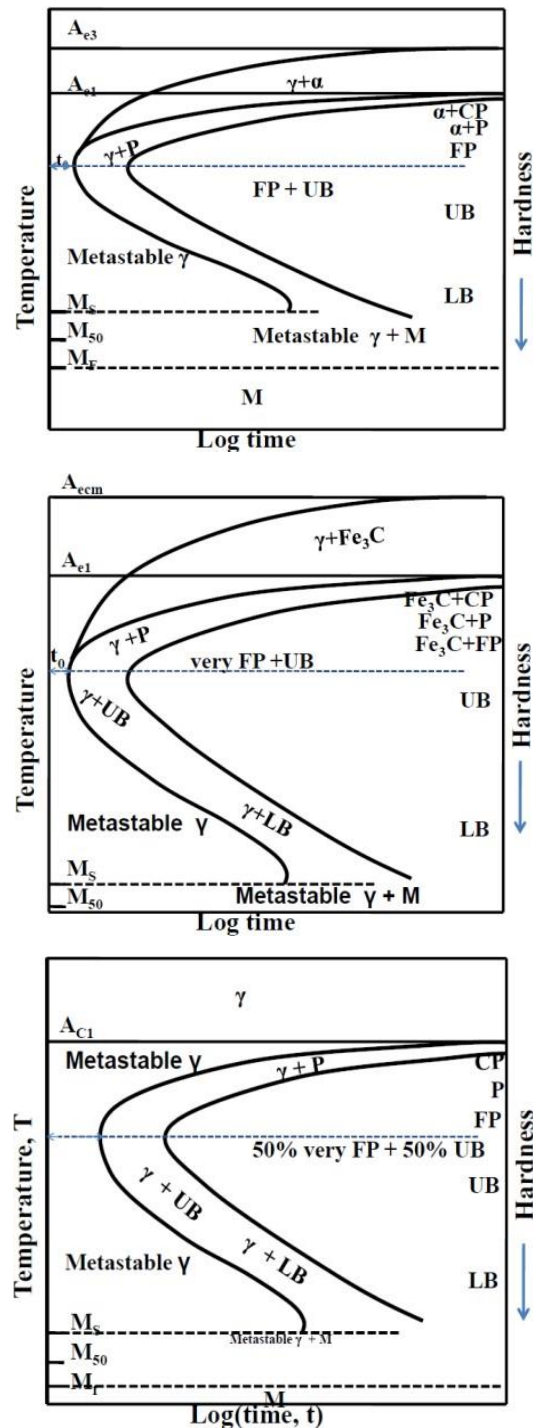


Figure 1. TTT diagrams for (a) hypoeutectoid, (b) eutectoid and (c) hypereutectoid steels

ASTM A 255 measures hardenability of steels. Hardenability is a measure of the capacity of a steel to be hardened in depth when quenched from its austenitizing temperature. Hardenability of a steel should not be confused with the hardness of a steel. The Hardness of a steel refers to its ability to resist deformation when a load is applied, whereas hardenability refers to its ability to be hardened to a particular depth under a particular set of conditions. Information gained from this test is necessary in selecting the proper combination of alloy steel and heat treatment to minimize thermal stresses and distortion when manufacturing components of various sizes.

Experimental Procedure:

First, a sample specimen cylinder either 100mm in length and 25mm in diameter, or alternatively, 101.6 mm by 25.4 mm is obtained. Second, the steel sample is austenitised. This is usually at a temperature of 800 to 900°C. Next, the specimen is rapidly transferred to the test machine (Fig. 2), where it is held vertically and sprayed with a controlled flow of water onto one end of the sample. This cools the specimen from one end, simulating the effect of quenching a larger steel component in water. Because the cooling rate decreases as one moves further from the quenched end, you can measure the effects of a wide range of cooling rates from vary rapid at the quenched end to air cooled at the far end.

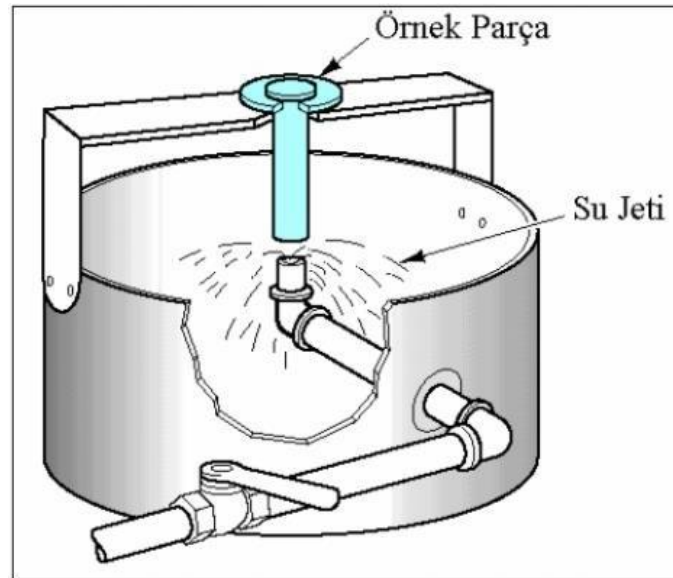


Figure 2. Schematic view of Jominy test

The hardness is measured at intervals along its length beginning at the quenched end. For alloyed steels an interval of 1.5mm is commonly used where as with carbon steels an interval of 0.75mm is typically employed.

And finally the Rockwell hardness values are plotted versus distance from the quenched end.

The Jominy Test data illustrates the effect of alloying and microstructure on the hardenability of steels.

Commonly used elements that affect the hardenability of steel are carbon, boron, Chromium, Manganese, Molybdenum, Silicon, and Nickel.

Carbon is primarily a hardening agent in steel, although to a small degree it also increases hardenability by slowing the formation of pearlite and ferrite. But this affect is too small to be used as a control factor for hardenability.

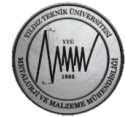
Boron can be an effective alloy for improving hardenability at levels as low as .0005%. Boron is most effective in steels of 0.25% Carbon or less. Boron combines readily with both Nitrogen and Oxygen and in so doing its effect on hardenability is sacrificed. Therefore Boron must remain in solution in order to be affective. Aluminum and Titanium are commonly added as "gettering" agents to react with the Oxygen and Nitrogen in preference to the Boron.

Slowing the phase transformation of austenite to ferrite and pearlite increases the hardenability of steels. Chromium, Molybdenum, Manganese, Silicon, Nickel and Vanadium all effect the hardenability of steels in this manner. Chromium, Molybdenum and Manganese being used most often.



Requested in the Test Report

- Draw Jominy curve for 1040, 1060, 4140 and 4340 steels depending on the distance from the end.
- Explain how the Grossman hardenability test is performed and the advantages and weaknesses compared to the Jominy experiment.
- Which mechanisms reduce the hardenability of steel when Al and Co are introduced? Explain.
- Which mechanisms increase the hardenability of steel when the other alloying elements except Al and Co are introduced? Explain.
- Why is the Jominy test not applied to high alloy steels? Explain.



8. CERAMICS EXPERIMENT

1. Aim of the Experiment

The aim of this experiment is to explain the fundamentals of ceramic production and preparation of a ceramic slurry. Raw material preparation, grinding kinetics and rheological behaviour of the ceramic slurry will be explained in detail.

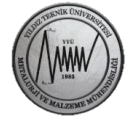
2. Theoretical Section

2.1. Preparation and the Rheology of a Ceramic Slurry

Drying of the droplets produces highly uniform, more or less spherical hollow granules (with a moisture content of typically 5.5 to 7%). This form of powder has high fluidity, facilitating accurate filling of the press dies and the subsequent pressing of quite large single tiles. A ceramic slurry includes the ceramic raw materials, water and auxiliary agents such as binders, deflocculants etc. In order to prepare an optimum composition, special tables are used which called as Seger Tables or Seger Rates. This Seger tables point out the ratios between the oxides which are present in the ceramic raw materials. Keeping the ratios constant is necessary while developing new compositions because every oxide has a different effect on rheology. Seger tables varies concerning the final product and the desired properties from the final product. Rheology is the science of fluidity. Fluidity can be explained by two main values which are viscosity and thixotropy. Viscosity is the value of the fluidity of a material, fluidity and viscosity has an inverse ratio between them. Thixotropy is the value of the change in viscosity with time. There are two main fluid groups which are Newtonian and Non-newtonian fluids. Newtonian fluids are just like water, their viscosity don't change with time. But for Non-newtonian fluids, viscosity changes with time. Viscosity of the Non-newtonian fluids decrease with the counting time. Ceramic slurry is a Non-newtonian fluid and it shows thixotropy property. For the rheological study of a ceramic slurry, terms like flocculation, deflocculation and deflocculant should be explained. For ceramics, if the viscosity is too low, the surface quality of the products will be low and there might be cracks on the surface. If the viscosity is too high, this will cause pinhole defects and difficulties for the transportation of the slurry (mobility). When it comes to thixotropy, it is also as important as viscosity. If the thixotropy is too high, drying time of the product will be long and if the thixotropy is too low, this will cause the product to become fragile.

2.2 Flocculation, Deflocculation, Deflocculant

When suspended in water, particles of an argillaceous material behave in two completely different mechanisms which is caused by the electrostatic charges present on the surface of the particles which can cause both attraction and repulsion. Regularly, in an acid environment, the particles are attracted to each other and this state is called as "flocculation". In an alkiline (basic) environment, the particles repulse each other and this state is called as "deflocculation". For the state of delocculation, the surface charges of the particles have been neutralized, this leads to the particles to remain as single separate units in suspension. Without the charges and without the attraction, there is no force holding the particles together, so this situation leads to a consequent decrease in viscosity. For the state of flocculation, the particles intend to form three-dimensional structures caused by the electrostatic attraction between them, so this situation leads to an increase in viscosity.



Deflocculants

Deflocculant term implies an additive which causes a decrease in viscosity when added. Deflocculants preclude flocculation by increasing the zeta potential between particles, which leads to the increase in repulsive forces between particles. There are several mechanisms for deflocculants to act in suspension, which can be enumerated as follows;

- Increasing the pH towards basic values by addition of bases or by hydrolysis.
- Supersession of flocculant cations which present in the double layer of clays along with alkaline cations.
- Adsorption of anions under electric field in order to achieve negative charge on particles.
- Addition of a preservative colloid.
- Elimination of flocculant ions which might be present in suspension, by precipitation or formation of coordination complexes.

Ordinarily, effects of deflocculants are submitted by a cooperation of above-mentioned mechanisms. Mechanisms do not depend on the nature of the deflocculant, it can either be organic or inorganic.

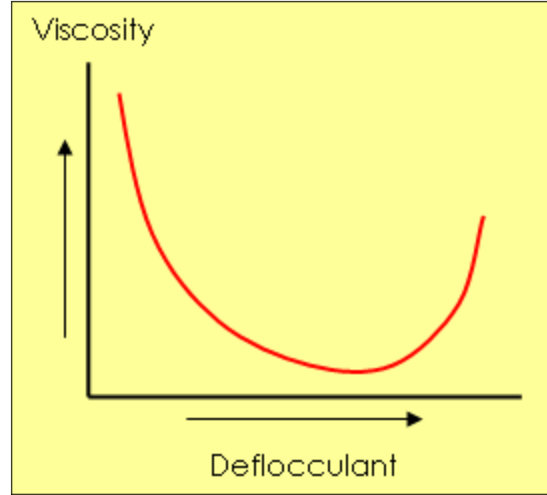
3. Experimental Section

3.1. Needed Instruments

Mill, Viscometer, Stirrer, Pyknometer, Sieve, Weighing Instrument

3.2. Application of the Experiment

First of all, raw materials are weighed and mixed regarding the composition. Then the necessary amount of water and deflocculant is added to the mix. Prepared slurry is grinded in ball mills. After the grinding process, density of the slurry is obtained by using a pyknometer. Concerning the density value of the slurry, corresponding weight is taken from the slurry and put through the 90 microns sieve. Oversize particles will give the average particle size of the grinded mix. After the determination of the average particle size, prepared slurry is mixed with a stirrer with a 700 rpm speed. During this period, in order to immobilize the viscosity level between 1-2 Poise (necessary value for floor tiles), deflocculant addition to the slurry is started. The amount of the added deflocculant is obtained by rule of thumb. After every addition, slurry is mixed for 3 minutes and viscosity value is determined by using an analog viscometer with a rotational speed of 20 rpm. Viscosity value of the slurry is optimized between 1-2 Poise without adding extra water in order to stabilize the solid concentration. To obtain the thixotropy, slurry is put in rest for 5 minutes after every viscosity measurement. Then viscosity is measured again, difference between these two viscosity values give the thixotropy. After the stabilization of the viscosity was achieved between 1-2 Poise, addition of the deflocculant is stopped. When the slurry reaches its final viscosity, added deflocculant will not effect the viscosity until a higher amount of deflocculant is introduced into the slurry. This higher amount of deflocculant act as not as expected and it will increase the viscosity of the slurry. So the proof for the reached value of the viscosity is the stability and the following increase in viscosity with the added deflocculant.



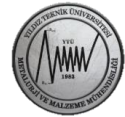
Şekil 1. Viskozite-İlave edilen deflokülant diyagramı

4. Results

As a result of this experiment, raw material preparation, grinding kinetics and rheological behaviour of a ceramic slurry is explained and shown experimentally.

Kaynaklar

- (1) RAHAMAN M. N., Ceramic Processing, 2006
- (2) BARNES H. A., Handbook of Elementary Rheology, 2000
- (3) WORRAL W. E., Ceramic Raw Materials, 1982
- (4) CICEK B., Ceramic Processing Methods Lecture Notes, 2015



9. OPTICAL PROPERTIES OF MATERIALS

PART 1 - INVESTIGATION OF OPTICAL PROPERTIES OF MATERIALS

OBJECTIVE: The objective of this experiment is to:

- A. measure the transmittance of ultraviolet and visible radiation by a set of standards optical materials.
- B. observe the transmittance of visible and ultraviolet radiation by optical materials and see the amount of radiation blocked out by these samples.

MATERIALS AND EQUIPMENT:

UV–Vis spectrophotometer, standard optical materials, alcohol, deionized water, drying paper

THEORETICAL BACKGROUND:

Spectroscopy is the study of objects based on the spectrum of color they emit or reflect. Scientists spend much time studying the interactions between matter and energy. Because there are several forms of energy and a large supply of matter, these studies have provided many measurements and much knowledge about the universe and its behavior. A study of electromagnetic energy with matter provides valuable and important information about molecular structure and properties. In fact, some of the most convincing evidence about atomic and molecular structure, and the origin and makeup of the universe have been obtained this way.

Light is electromagnetic radiant energy. Depending upon the point of view, light can be thought of as having either wave properties or particle properties. The argument as to whether light behaves as waves or particles persisted for centuries. Wave–particle duality is a theory that proposes that all matter exhibits the properties of not only particles, which have mass, but also waves, which transfer energy. A central concept of quantum mechanics, this duality addresses the inability of classical concepts like "particle" and "wave" to fully describe the behavior of quantum-scale objects. The idea of duality originated in a debate over the nature of light and matter that dates back to the 17th century, when Christiaan Huygens and Isaac Newton proposed competing theories of light: light was thought either to consist of waves (Huygens) or of particles (Newton). Through the work of Max Planck, Albert Einstein, Louis de Broglie, Arthur Compton, Niels Bohr, and many others, current scientific theory holds that all particles also have a wave nature (and vice versa). According to the wave theory, electromagnetic radiation is composed of both electric and magnetic fields whose waves vibrate in mutually perpendicular planes. It is the electric field of light interacting with the electrons of matter which produces observable properties of a substance.

Two fundamental characteristics are associated with any wave – the wavelength and the frequency. The wavelength, λ (Greek letter, lambda), is measured from the crest of a wave to the adjacent crest (see Fig. 1). Wavelengths range from very small (measured in nanometers, 10^{-9} m) to quite large, several meters. The frequency is the number of waves passing a point in unit time and is designated ν (Greek letter, nu). Frequency can be expressed in cycles (or vibrations) per second. Wavelength and frequency are inversely proportional to each other; the shorter the wavelength, the more waves pass a point in a given time and thus the higher the frequency. Similarly, the longer the wavelength, the lower the frequency.

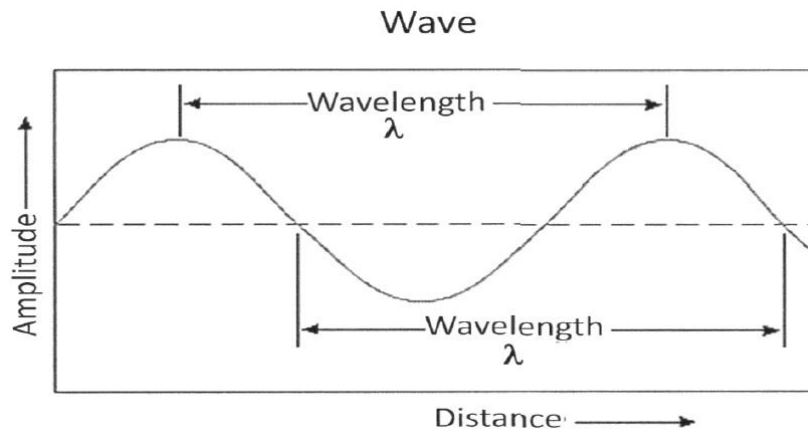


Fig. 1: The description of wavelength

Wavelength and frequency are related by the speed of light ($c = 2.998 \times 10^{10}$ cm/sec).

$$c = \lambda\nu$$

Another important relationship is that between these quantities and the energy of light.

$$E = h\nu \text{ or the equivalent } E = hc / \lambda$$

Where: h is Planck's constant (6.626×10^{-34} Joule.sec)

The greater the energy of the radiation, the shorter its wavelength and the higher its frequency; the smaller the energy of radiation, the longer its wavelength and the lower its frequency.

Relationship of Light Absorbed or Transmitted and Observed Color

Light from the sun is composed of a continuum of energies and thus, of a continuum of wavelengths and frequencies. Most of the electromagnetic radiation continuum is invisible to humans; the portion we perceive is referred to as visible light. Wavelengths of visible light extend from about 800 nm (8.0×10^{-5} cm) to about 400 nm (4.0×10^{-5} cm). Fig. 2 shows the entire wavelength range of the electromagnetic spectrum arbitrarily divided into regions called bands and the portion occupied by visible light.

It is against the high energy Ultraviolet (UV) radiation that sun screen lotions are formulated to protect our skin in the outdoors. Our skin perceives the low energy infrared (IR) radiation only as heat. The lamps placed over food in cafeterias emit most of their energy in the red part of the Infrared region, keeping the food warm.

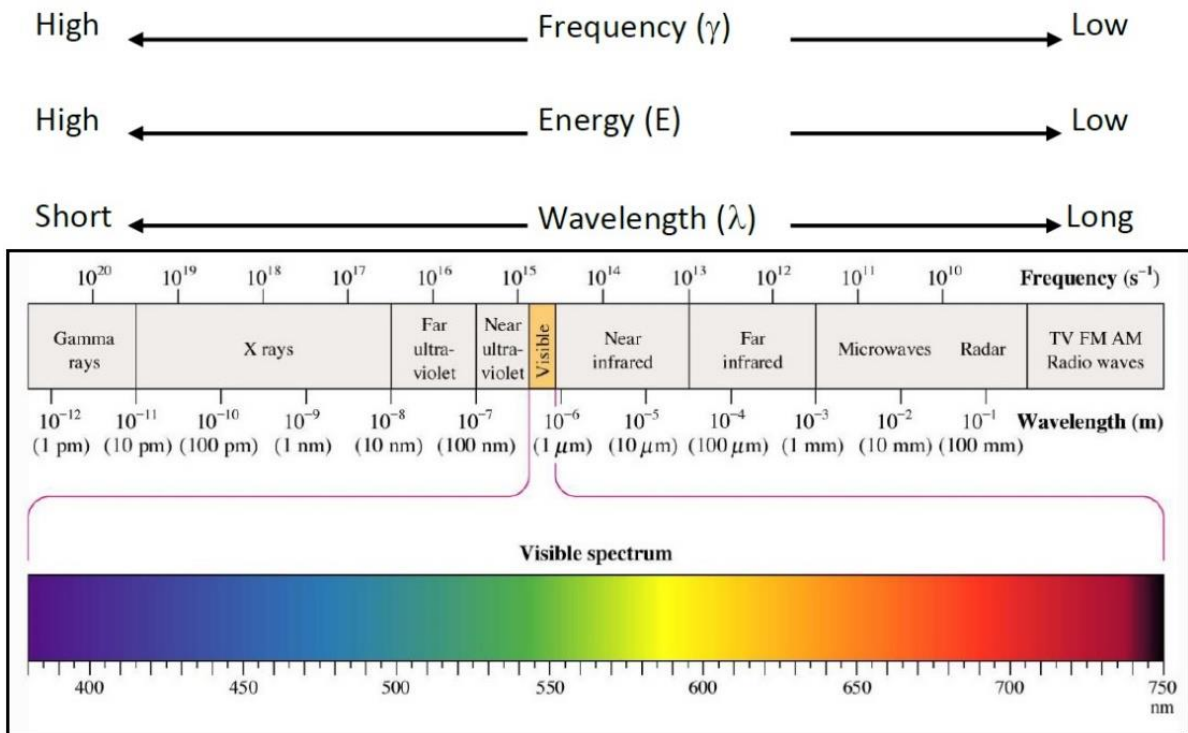


Fig. 2: Electromagnetic Spectrum

If little or none of the visible light striking our eyes is not absorbed prior to striking the eye, the color appears white. If this band of visible light is separated into narrow bands of wavelengths by a prism, we perceive the component colors. Isaac Newton divided the visible spectrum into seven color bands ranging in sequence starting with the shortest wavelengths (left to right in Fig. 2 above): violet, indigo, blue, green, yellow, orange, red.

When light impinges on a substance, one or more combination of things can happen to the light. The light can be scattered, reflected, transmitted, or absorbed by the substance. The absorbed light energy causes such changes as atomic and molecular rotation, vibrations, and electron transitions to higher energy levels. As a result of this absorption, our eyes or specially designed instruments may sense phenomena such as heat, fluorescence, phosphorescence, or color. Modern instrumentation can record these phenomena to a very high degree of precision.

The simplest cases are those where all incident light directed at a substance is either absorbed or transmitted. If a substance absorbs all wavelengths in the visible range, none of the light is reflected back to our eyes and the substance appears black. If the substance absorbs none of the incident visible light, it appears white (all light reflected) or colorless (all light transmitted). Colorless substances usually absorb in the UV or IR regions of the spectrum, on either side of the visible range.



Table 1: The wavelengths of colors observed, and colors absorbed

Wavelength Absorbed (nm)	Color Absorbed	Color Observed
410	violet	yellow-green
430	blue-violet	yellow
480	blue	orange
500	blue-green	red
530	green	purple
560	yellow-green	violet
580	yellow	blue-violet
610	orange	blue
680	red	blue-green
720	red-purple	green

If a substance absorbs light principally in one wavelength range (generally, a number of wavelengths on both sides of the principal absorption are also absorbed, so a broad absorption band results), the color perceived will be a mixture of all the wavelengths which are not absorbed. For example, the indigo dye in blue jeans has its maximum absorbance in the 500 – 650 nm range. Because this absorbance is in the red-to-green region, the wavelengths which are not absorbed are in the 400-500 nm range, thus, the color observed would be blue-violet. An aqueous solution that appears yellow, a narrow range around 550 nm, means that wavelengths on either side of yellow, primarily blues, greens and reds, are being absorbed. A green solution would be expected to transmit green wavelengths, while blocking blues, yellows, and reds. Table 1 is a summary of the relationship between the wavelengths of colors observed and colors absorbed.

Complementary Colors:

A more fundamental grouping than Newton’s are the systems of 3 primary colors and their secondary complementary colors. Complementary colors are pairs of colors which, when combined in the right proportions, produce white or black. When placed next to each other, they create the strongest contrast and reinforce each other. They are widely used in art and design and especially in video monitors, such as television screens. In painting, which uses subtractive colors, the traditional primary–secondary complementary color pairs, described since at least the early 18th century, were red–green, yellow–violet, and blue–orange. The more accurate RGB (red, green, blue) color model, invented in the 19th century and fully developed in the 20th century, uses additive color combinations of red, green, and blue light against a black background to make the colors seen on video screens. In the RGB color model, the light of two complementary colors, such as red and cyan, combined at full intensity, will make white light, since two complementary colors contain light with the full range of the spectrum. If any of these three colors is absorbed from white light, the complementary color is observed. The proper combination and intensities of the three primary colors create every conceivable color and shade. Table 2 below is a summary of the primary-secondary complimentary colors used in the RGB model.

Table 2: Primary and Secondary Complementary Colors

Complimentary Colors and Wavelengths of Maximum Absorption (nm)				
Primary			Secondary	
Red	690	↔	Cyan (Green-Blue)	488
Green	520	↔	Magenta (Red-Blue)	(non-spectral)
Blue	480	↔	Yellow (Red-Green)	580

Spectroscopy:

Spectroscopy is a basic analytical technique and research tool that utilizes the interaction between matter and electromagnetic energy. A spectrometer is an instrument that separates electromagnetic radiation according into wavelengths, passes these separated wavelength bands through a sample, and detects the intensity of the transmitted light. In analyzing a new sample, a scientist first determines the sample's absorbance spectrum. The absorbance spectrum is a plot of absorbance vs wavelength and shows how the absorbance of light depends upon the wavelength of the light.

The absorption spectrum is characterized by the wavelength of maximum absorption (λ_{max}) at which the absorbance is the greatest (see Fig. 3 below. The value of λ_{max} is important for several reasons. It is used in order to obtain the highest sensitivity and to minimize deviations from Beer's Law (see development below). It is characteristic of each unique compound providing information on the electronic structure of the compound.

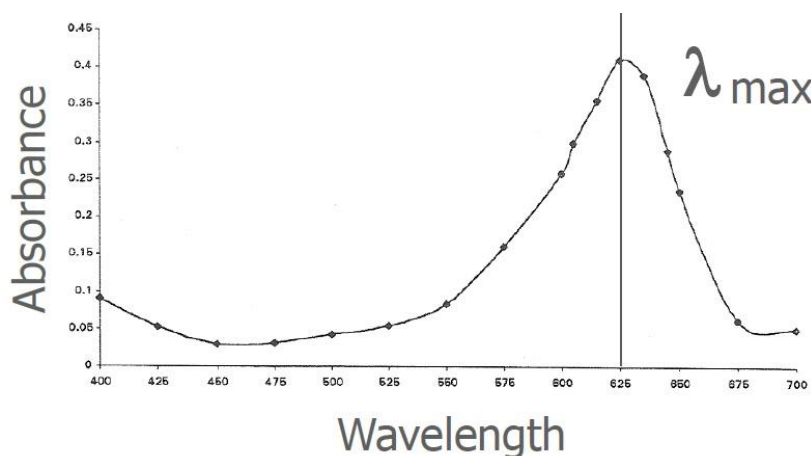


Fig. 3: The example of an absorption spectrum

All spectrometers have the following fundamental parts: a source or radiant energy, a prism or grating to isolate radiant energy to narrow wavelength regions, a device for holding the sample, and a detector for measuring light intensity. Sophisticated instruments include automatic recorders, digital readouts, computer interfaces, and arrays of detectors that allow the user to analyze a wider range of wavelengths.

The Beer-Lambert Law:

The Beer–Lambert law, also known as Beer's law, the Lambert–Beer law, or the Beer– Lambert–Bouguer law (named after August Beer, Johann Heinrich Lambert, and Pierre Bouguer) defines the mathematics relating the absorption of light to the properties of the material through which the light is traveling. The derivation of the equations used with the law involves two principle variables.



Transmissivity:

The amount of light absorbed as it is transmitted through the substance. It is defined as the ratio of the light intensity leaving the sample to the intensity entering the sample:

$$T = \frac{I}{I_0}$$

Spectrometers measure the percent (%T) transmittance of light passing through the sample.

$$\%T = \left(\frac{I}{I_0} \right) \cdot 100$$

Absorbance:

Absorbance is the amount of light absorbed expressed in logarithmic terms. It is defined as the negative logarithm (base 10) of the Transmittance.

$$A = -\log_{10} T = -\log_{10} \left(\frac{I}{I_0} \right)$$

The law states that there is a logarithmic dependence between the transmissivity of the light through the sample and the product of the “absorption coefficient (α)” of the substance and the distance (l) the light travels through the material. The absorption coefficient is a measure of the rate of decrease in the intensity of electromagnetic radiation (as light) as it passes through a given substance. The absorption coefficient can, in turn, be rewritten as a product of the molar absorptivity (ϵ) and the molar concentration (c) of the absorbing species. Molar absorptivity (also called the molar absorption coefficient or molar extinction coefficient) is a wavelength-dependent intrinsic property of the species and is a measurement of how strongly a chemical species absorbs light at a given wavelength. Incorporating these terms into the expression for absorbance results in the following:

$$A = -\log_{10} T = -\log_{10} \left(\frac{I}{I_0} \right) = \alpha \cdot l = \epsilon \cdot c \cdot l$$

Where: A is the measured absorbance (absorption units, technically unitless)

T is the amount of light absorbed passing through sample (transmittance)

I is the intensity of the radiation leaving the sample

I₀ is the intensity of the incident radiation

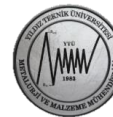
α is the absorption coefficient

l is the path length of the sample cell

ϵ Epsilon is the wavelength-dependent molar absorptivity with units of L mol⁻¹ cm⁻¹

c is the analytic concentration (Molarity) with units of mol/L

EXPERIMENTAL STUDY:



Please be careful while using the equipment in the lab. Switch off all equipment and tidy the lab before you leave.

Many sunglasses on the market today are advertised as being able to protect your eyes from the harmful effects of ultraviolet radiation by being "blue blockers" or having ultraviolet-resistant coating. The purchase tags on most sunglasses state the percentage of ultraviolet radiation that they can block. Are these claims accurate? Are they measurable? This experiment is designed to help you find out.

The visible portion of the electromagnetic spectrum ranges from approximately 700 nm to 400 nm. This is the light we see as the familiar ROYGBIV (red, orange, yellow, green, blue indigo, and violet) colors of light. The ultraviolet portion of the electromagnetic spectrum ranges in wavelength from approximately 400 nm to 10 nm. The portion of the UV spectrum nearest the visible spectrum, from about 400 to 320 nm, is sometimes called UVA. The radiation from 320 to 290 nm is called UVB. The remaining portion of the UV spectrum is known as UVC.

The waves in the ultraviolet portion of the spectrum are relatively high in energy. You are familiar with the effects these waves have on the cells of your skin when you get a tan or a sunburn. The lower energy UVA waves are mostly responsible for the tan, while the higher energy UVB causes the sunburn.

.....700nm.....400nm.....320nm...290nm....10nm.....

←Infrared Visible UVA UVB UVC x-rays→

-----INCREASING ENERGY-----→

Your eyes can be affected by the ultraviolet radiation just as your skin can. On Earth, the atmosphere is able to screen out most wavelengths below 300 nm. Those UVA and UVB wavelengths that penetrate the atmosphere can be prevented from affecting the eyes by sunglasses that are manufactured to block this radiation.

Sunglasses are made of glass or plastic that will allow much of the visible light to be transmitted and can be designed to absorb ultraviolet radiation. Since we are interested in the amount of ultraviolet radiation that passes through the sunglasses into your eyes, we will measure transmittance of the visible and ultraviolet light through lenses. Absorbance and transmittance are terms which refer to the amounts of radiation "soaked up" or "allowed to pass through" the lenses. To conduct this experiment successfully, you should become familiar with the basics of ultraviolet spectroscopy and the difference between absorbance and transmittance of light. In this experiment you will use the PG T80+ Spectrophotometer. This instrument provides sources of both visible and ultraviolet radiation.

PROCEDURE

A. To Run % Transmittance of Standards

1. Turn on spectrophotometer from power button (at the back of the device). It will take approximately ten to fifteen minutes for the instrument to warm up.
2. Run "UVWin Software" from desktop and press "OK".
3. From left frame select "Spectrum".
4. From menu select "Measure/Parameters Settings" to enter measurement parameters.



5. From “**Measure**” tab select Absorbance (%Abs) or Transmittance (%T) mode to measure, from “**Scan Parameters**” tab adjust the starting and ending wavelength.
6. From “**Instrument**” tab select the lamps which will be used, turn off the D2 lamp if not necessary (if UV region will not be covered).
7. Press “**OK**” to save measurement settings.
8. Press “**Baseline**” to run the measurement without any sample to perform baseline correction. The screen will display 100 %T or 0 %Abs if correction is completed successfully.
9. Place the standard glass sample into the sample holder.
10. Replace the black cover and instrument chamber cover and press “**Start**”.
11. When scanning has finished, press “**Yes**” to save scanning results.

B. To Run % transmittance of glasses

1. By doing Part A. Steps 1-11, the spectrophotometer should be programmed to do scans of the glasses. If you have changed any of the parameters from Part A., then repeat Steps 1-11.
2. Gently place your glasses in the spectrophotometer under the supervision of _____ the lab assistant.
3. Close the instrument chamber cover and press “**Start**”.
4. When scanning has finished, press “**Yes**” to save scanning results.

POST-LAB QUESTIONS:

1. Which kind of ultraviolet radiation contains the most energy? What is the range of wavelengths of this radiation?
2. Which form of ultraviolet radiation is most damaging to your eyes? What is the range of wavelengths for this radiation?
3. Which type of radiation should sunglasses block?
4. Describe the difference between absorbance and transmittance.
5. An absorbance spectrum shows a peak at 540 nm. What does this mean?
6. A transmittance spectrum shows a peak to 80% between 480 nm and 524 nm. What does this mean?

REFERENCES

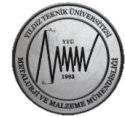
1. Williams, John E.; Trinklein, Frederick E.; Metcalfe, Clark H. (1984). Modern Physics (p. 287-288). New York: Holt, Rinehart, and Winston.
2. Pelczar, Michael J.; Chan, E. C. S.; Kreig, Noel R. (1986). Microbiology (p. 480). New York: McGraw-Hill Book Company.
3. Selinger, Ben. (1989). Chemistry in the Marketplace (p. 121). Sydney: Harcourt Brace Jovanovich.
4. Questions and Answers About UV Coatings. (1992). Lenscrafters® Pamphlet.



MSE3961 Laboratory-I Experiment Booklet



5. Pasachoff, Jay A. and Kutner, Marc L. (1978). University Astronomy (p. 630-631). Philadelphia: W.B. Saunders Company.
6. 1982-83 CRC Handbook of Chemistry and Physics (p. E-201). Cleveland: CRC Press.
7. Peters, Dennis G.; Hayes, John M.; Heiftje, Gary M. (1974). Separations and Measurements: Theory and Practice of Analytical Chemistry (p. 616). Philadelphia, W. B. Saunders Company.



10. PYROMETALLURGY EXPERIMENT

1. OBJECTIVE OF THE EXPERIMENT

The objective of this experiment is to produce concentrated iron ore pellets with suitable physical and chemical properties for and to investigate the thermodynamic and kinetic aspects of the solid state reduction of ferrous raw materials using carbon (carbothermic reduction).

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].

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°C 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. [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°C - 1100°C). 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 $\leq 4 \text{ g/cm}^3$.

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 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:

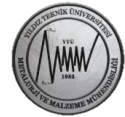
- high iron content (65-67% Fe),
- superior resistance to crumbling and dusting due to its high strength and transport properties,
- good gas permeability due to their close size and uniform gas distribution,
- good reducibility properties due to high porosity.

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].

Pellet Production

50-80% of the grain sizes of the iron concentrate used in pellet production should be below 0.045 mm (325 mesh). The process for conventional pellet production consists of the following four sub-applications:

- 1- Threshing
- 2- Production of Wet Pellets
- 3- Drying
- 4- Thermal Hardening



1. Threshing

The desired blend is prepared by adding an appropriate amount of binder of iron ore. Studies have revealed that in order to cover the surfaces of the concentrates with water, the water ratio should be 7-10% and the binder ratio should be 0.5-1.5%.

2. Production of Wet Pellets

The prepared mixture is added to the device where the agglomeration process will be carried out. Agglomeration begins with the binder effect due to the rotational movement of the device. Pellet production is completed with the following stages:

- i. Nucleation (A small number of particles coming together to form the first nucleus.)
- ii. Transition (From nucleus to pellet)
- iii. Reaching of the produced to pellets to desired dimensions.

3. Drying

It is the stage of partial purification of the moisture contained in the wet pellet obtained by subjecting it to a pre-heating. During this process, care should be taken not to apply a process that will cause the pellet to crack, and the humidity, which is around 7-10%, should be removed.

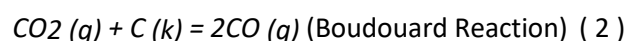
4. Thermal Hardening

The pellets placed in the ceramic boat in an oxidizing atmosphere are baked in a furnace at a temperature between 1200-1350 °C, and they reach the desired strength values. The pellets are baked on a sintering grid, in a shaft furnace or in a rotary kiln. The fuel can be coal dust, liquid or gas. Pellet strength at the end of cooking is at least 150-350 kg. It should be enough to withstand the compression load in the range. The resulting pellet will provide the blast furnace with rechargeable properties.

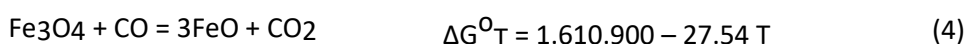
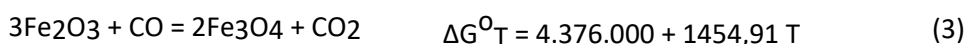
Thermodynamic Investigation of Reduction Reaction

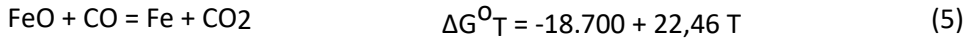
The carbothermic reduction of iron oxides to metallic iron, is accomplished by removal of the oxygen contained in the raw materials by deterioration of the iron-oxygen-carbon thermodynamic equilibrium to the reduction condition. In this condition, iron oxides reduce to metallic iron by the result of 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 CO₂ gas with carbon, due to the fact that CO₂ gas, produced by combustion of carbon, is unstable at high temperatures (see Ellingham Diagram).



The reduction of hematite to iron with CO/CO₂ gas mixture, takes place in three stages. The temperature-dependent empirical expressions (3), (4), and (5) of the standard free energy change ($\Delta G^\circ T$) for these reactions and reactions are given below.





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

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

$$\Delta G^{\circ}_T = -RT \ln K_p \quad (7)$$

$$K_p = \frac{a_{\text{Fe}_3\text{O}_4}^2 \cdot P_{\text{CO}_2}}{a_{\text{Fe}_2\text{O}_3}^3 \cdot P_{\text{CO}}} \quad (8)$$

When Fe₃O₄ and Fe₂O₃ are assumed to be pure, their activities are equal to "1". In this case;

$$\Delta G^{\circ}_T = -RT \ln \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = RT \ln \frac{P_{\text{CO}}}{P_{\text{CO}_2}} \quad (9)$$

From this, the $\left(\frac{P_{\text{CO}}}{P_{\text{CO}_2}}\right)_D$ ratio which balances the reduction reactions at the T₁ temperature can be calculated. The basic thermodynamic condition for the reduction of iron oxides is as follows for each reaction.

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

$$\left(\frac{P_{\text{CO}}}{P_{\text{CO}_2}}\right)_{\text{Ortam}} > \left(\frac{P_{\text{CO}}}{P_{\text{CO}_2}}\right)_{\text{Denge}} \quad (11)$$

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

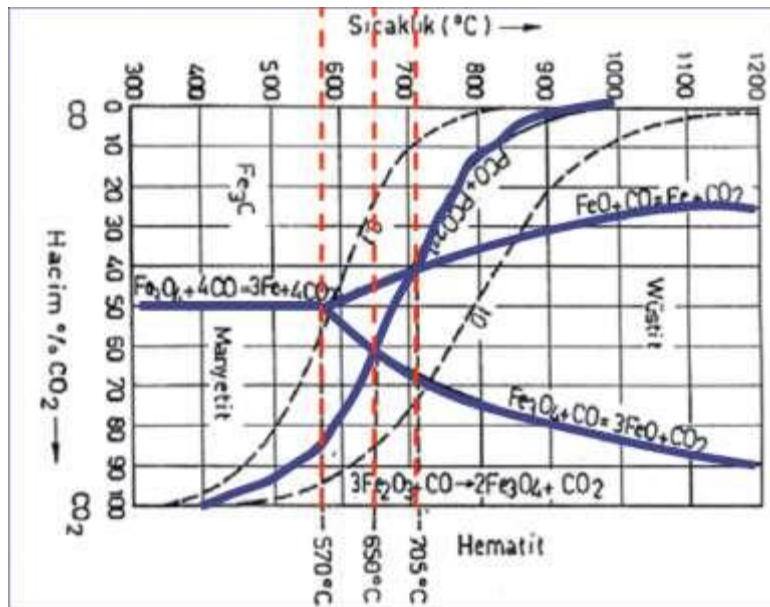


Figure 4.1 Bauer-Glaessner diagram and Boudouard curves

According to Figure 1, the metallic iron reduction of iron oxides at a total pressure of P_{co} + P_{co2} = 1 atm is only possible above 705 °C, under 705 °C, hematite to magnetite and magnetite to wüstite transformation is possible. It can be seen from Figure 1 that a magnetite-wüstite 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



PCO + PCO₂ 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;

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

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

k = reaction rate constant (temperature dependent)

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

n = reaction ratio

concentration.

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.

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

In this equation, EA 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.

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

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 (-EA / R) (Figure 2).

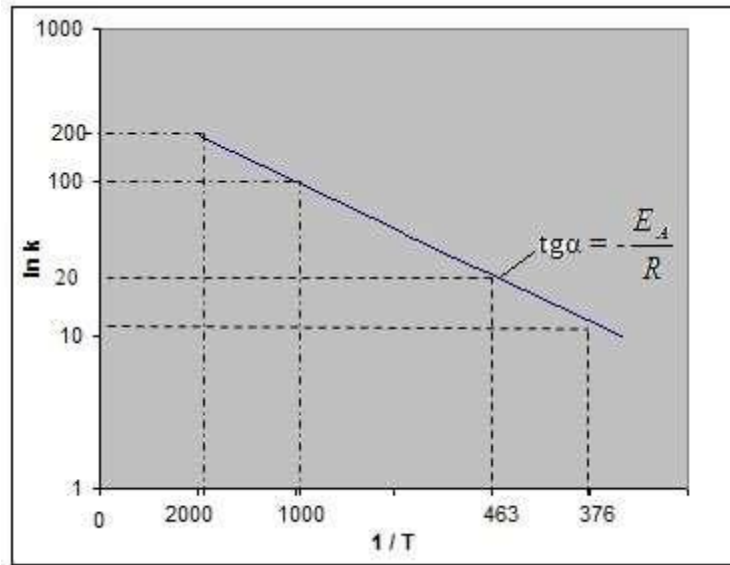


Figure 4.2 Change of reaction rate with temperature

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:

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

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

W_o = Initial weight

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

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.

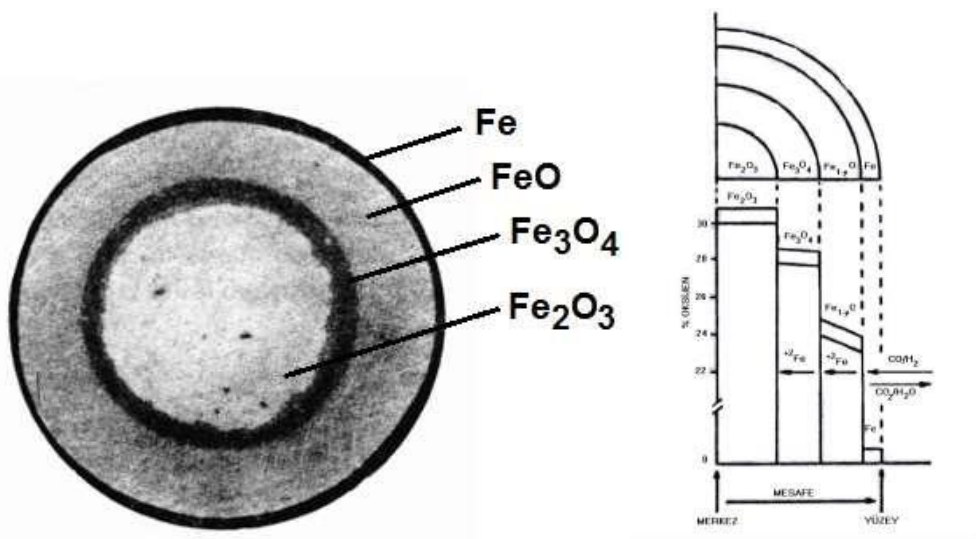




Figure 4.3 Schematic representation of the reduction of the hematite particle and the topochemicality in reduction [5, 6, 8].

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].

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. 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.

	Fe₃O₄	SiO₂	Al₂O₃	S	Mn	CaO	MgO	K₂O	Na₂O	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:

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

5. ASSIGNMENTS AND REQUESTS

- 1) Write down the aim and procedure of the experiment.
- 2) Calculate the required amount of theoretical coal.

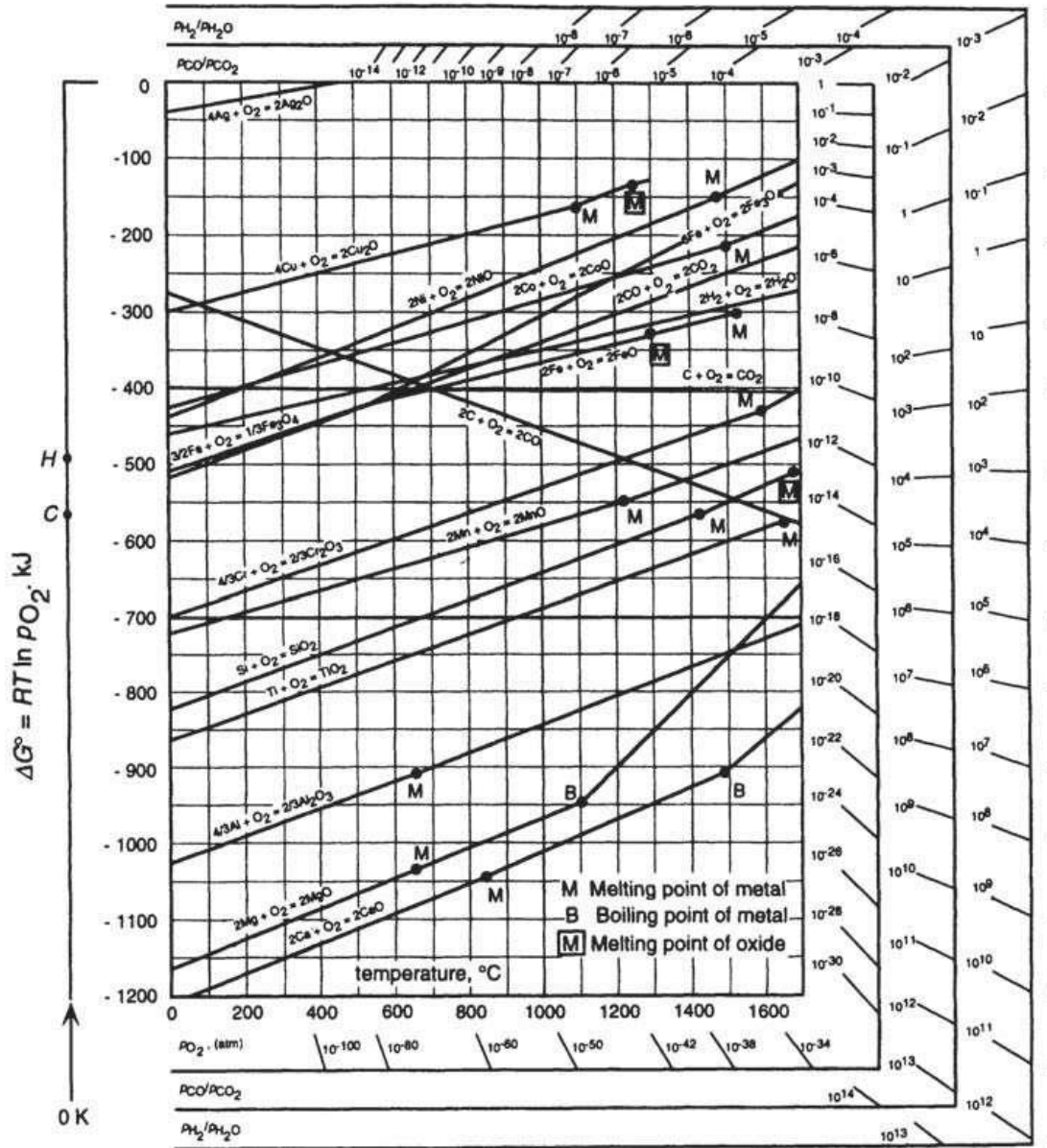


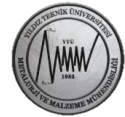
- 3) Draw the variation of the reduction ratio with time and evaluate the graph.
- 4) Calculate the instantaneous reduction rate (dR / dt) at 5th, 10th and 20th minutes.
- 5) For the reduction of ferrous raw materials, under what conditions is the reduction kinetics controlled by chemical reaction, diffusion 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 $PCO + PCO_2 = 1$ atm environment and name the zones. (Bauer-Glaesner diagram plotted against % CO amount).

6. REFERENCES

- [1] www.worldsteel.org, Uluslararası Demir ve Çelik Enstitüsü (IISI).
- [2] www.dcu.org.tr, Demir Çelik Üreticileri Derneği.
- [3] Doğu Akdeniz Kalkınma Ajansı Demir Çelik Sektör Raporu 2014.
- [4] BISWAS, A.K., Principles of Blast Furnace Ironmaking, Cootha Publish House, Brisbane, Australia, 1981.
- [5] ROSENQVİST, T., "Principles of Extractive Metallurgy", Mc Graw-Hill Book Co., 2nd Ed. 1983.
- [6] BOR, F.Y., "Ekstraktif Metalurji Prensipleri" Kısım I ve II, İTÜ, 1985.
- [7] www.midrex.com, Midrex Technologies, Inc.
- [8] ERSUNDU, A.E., "Yerli Demir Cevherlerinin Sünger Demir Üretimine Uygunluğunun Araştırılması", İTÜ, Fen Bilimleri Enstitüsü, İstanbul, 2007.
- [9] BİROL B., "Divriği Pelet Konsantresinden Kompozit Pelet ve Demir Tanesi Üretimi", YTÜ, Fen Bilimleri İstanbul, 2007.
- [10] HABASHI, F., Kinetics of Metallurgical Processes, Métallurgie Extractive Québec, Sainte-Foy, Québec, 1999.
- [11] AYDIN, S., Metalurji Kinetiği Ders Notu, 1994.
- [12] ŞEŞEN, K., Metalurjik Süreçlerin Kinetiği, İTÜ Kimya Metalurji Fakültesi Ofset Atölyesi, İstanbul, 1998.
- [13] RAY, H.S., Kinetics of Metallurgical Reactions, Oxford, New Delhi, 1993.

Ellingham Diagram





11. POLYMER EXPERIMENT

Objective: 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.

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.

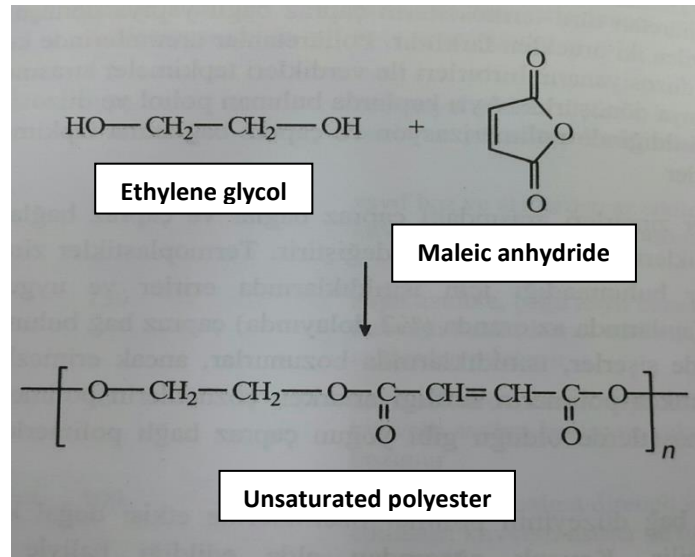


Figure 1: Synthesis of unsaturated polyester.

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 ($\text{CH}_2 = \text{CHR}$) such as a solvent 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 α -methyl styrene are other monomers used for cross-linking of unsaturated polyester resins.

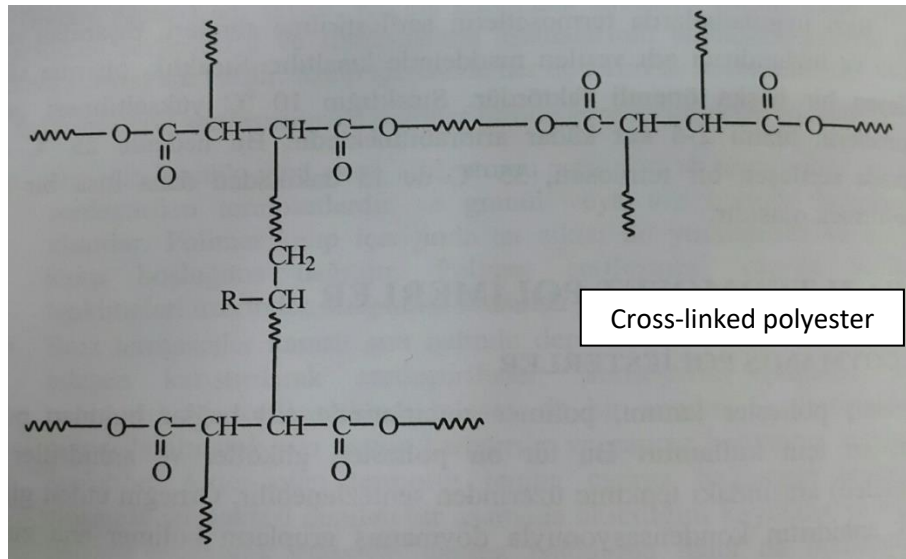


Figure 2: Vinyl monomer-cured cross-linked polyester.

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.

For more information:

- <https://www.youtube.com/watch?v=HiEzIDLLcu4>
- https://www.youtube.com/watch?v=O_rINqV3JY&t=43s
- <https://www.youtube.com/watch?v=LawOeMvCg6I>

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.

Chemical materials and equipment to be used:

<u>Resin:</u>	Unsaturated polyester / styrene mixture
<u>Initiator:</u>	Methyl ethyl ketone (MEK) peroxide
<u>Accelerator:</u>	Cobalt naphthenate
<u>Other materials:</u>	Molds, plastic cups, wooden spatula, mixer, thermometer, chronometer and plastic pipette.

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 naphthenate 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.

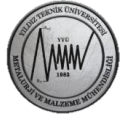
Results and discussion:

- 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.

References

Bilyeu, B., Brostow, W., & Menard, K. (tarih yok). Epoxy Thermosets and Their Applications I: Chemical Structures and Applications. *Journal of Materials Education*, 21(5&6), 281-286.

Saçak. (2012). *Polimer Kimyası*. Ankara: Gazi Kitabevi.



Saçak, M. (2012). *Polimer Teknolojisi*. Ankara: Gazi Kitabevi.

Stickney, K., Burnell, J., & Wyeth, J. (2019). Synthesis of a Crosslinked Epoxy Resin Medallion in the Organic Chemistry Laboratory. *World Journal of Chemical Education*, 7(4), 232-241.



NOTLAR