YILDIZ TECHNICAL UNIVERSITY

METALLURGICAL AND MATERIALS ENGINEERING DEPARTMENT

MSE3961 LABORATORY I

EXPERIMENTAL BOOKLET

2023-2024
FALL

TABLE OF CONTENTS

IMPORTANT INFORMATIONS

1) 8 experiments will be conducted throughout the semester.

2) Only in case of not being able to participate in the experiment for a week will be able to participate in the make-up experiment. A student who does not attend the trial for more than two weeks will be considered absent.

3) There will be no tests during the midterm week.

4) Tests not entered will be evaluated as zero.

5) Different experiments will be carried out for designated groups every week, and all students are required to participate in group experiments with their student numbers in the laboratory program shared on the department page.

6) Experiments will be carried out face to face and in the laboratory where each experimental subject is relevant.

7) There will be a short exam (Quiz) before the experiment. For this reason, you are expected to look at the purpose of the experiment, test process, equipment, and chemicals to be used in the experiment in your test sheets.

8) After the experiment, you are expected to write an experiment report in the specified format on the subject observed, discussed, and learned during the experiment. You must submit your experiment report to the instructor to whom the experiment relates on time.

9) You must bring your **own laboratory coat, latex gloves, laboratory glasses and mask** when coming to the experiments. You must have laboratory safety equipment with you to participate in the experiment.

EXPERIMENT 1: MECHANICAL TESTS

PART 1: TENSILE TEST

1.1 PURPOSE OF THE EXPERIMENT

- Tensile testing is performed to determine essential design information about the strength of materials and to classify materials according to their properties. Tensile test is the pulling of a test sample prepared according to standards on a single axis, at a certain pulling speed and at a constant temperature, until it breaks. During the test, the elongation values resulting from the force or tension applied to the tensile sample prepared according to the standards are recorded.

1.2 THEOROTICAL INFORMATIONS

Samples to be subjected to tensile testing must have all the properties of the material they represent. Therefore, the region where the sample is taken and the way it is collected and prepared are of great importance. While preparing the sample, care should be taken to avoid any changes in the material properties it represents. Excessive temperature formation should be prevented during production, and effects resulting from deformation should be eliminated. The shape and dimensions of the sample to be subjected to tensile testing are specified in the standards. For this reason, in order to ensure the reliability and comparability of the test results, the experiments should be carried out with samples prepared according to standards. Depending on the material to be taken, the cross-section of the tensile sample may be circular, square, rectangular, ring-shaped, and even in some cases special profile-shaped. Turkish standards have standardized tensile samples according to their shapes and sizes in TS EN ISO 6892-1.
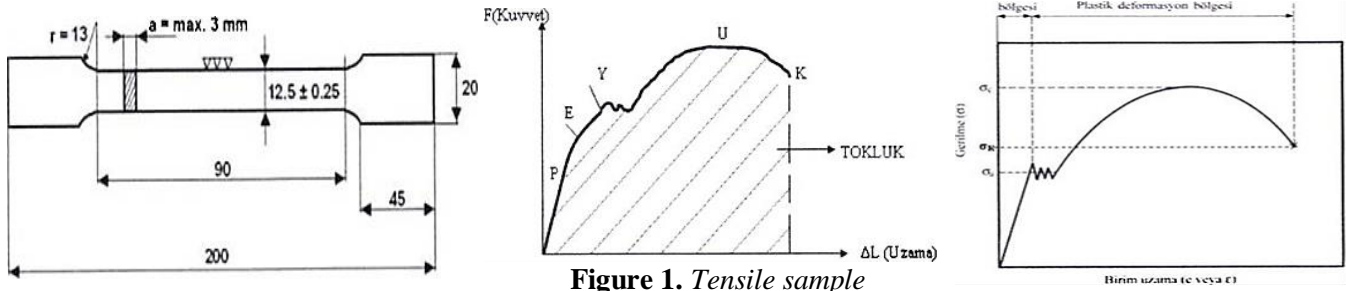

Figure 1. *Tensile sample dimensions, stress-strain diagram for rectangular cross-section metal materials and tensile diagram of a low carbon mild steel.*

The pulling device is mainly; It consists of two jaws that can move up and down relative to each other, to which the test piece is attached, and units that give movement or force to them and measure these two quantities. By moving one of the jaws at a constant speed, varying amounts of tensile force is applied to the test piece and the elongation corresponding to this force is recorded. At small force levels, the amount of extension is directly proportional to the force. The material is in elastic behavior; That is, when the force is removed, the elongation is reset. This character continues until point P. The proportionality limit changes the slope of the linear function after P. However, elastic behavior continues. Elastic behavior ends at point E "Elastic Limit". Permanent after E; In other words, it can take too much force and plastic deformations begin. When the force is reduced, it follows a path parallel to the linear function. However, where the force is zero, the deformation is no longer zero, a certain plastic deformation remains.

If the material continues to be loaded, it will flow at point Y. At the yield point, a large amount of plastic deformation occurs while the force is the same. The flowing material undergoes "work hardening" and becomes more durable. By increasing the force on this material, point U is reached. Point U is the "maximum stress" point, where local contractions begin in the material cross-section. This is called "necking" of the material. Necking also causes the material to undergo work hardening and the material can take on higher stresses; However, as the cross-sectional area narrows in the neck region, the net force it carries decreases. The sample usually moves uncontrollably to point K and breaks there. The area under the force-extension curve equals the energy required to degrade that sample; It is called satiety. The force-extension curve is then rescaled. Elongations are converted to "unit-extension" by dividing by the initial length of the material. Likewise, the "tension" is calculated by dividing the force by the initial cross-sectional area of the sample and the vertical axis is scaled again.
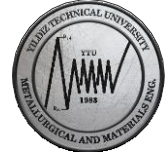
Definitions

Stress(σ): It means the load acting on unit area and is calculated by the formula: $\sigma = \dfrac{F}{A0}$

Unit Strain (ε): The ratio of the length change that occurs when a force is applied to the material to the initial length before the force is applied: $\varepsilon = \dfrac{\Delta L}{L0}$

Elasticity Modulus (E): It is the measure of the strength (strength) of the material. It is a result of the linear relationship between unit elongation and normal stress (tensile or compressive stress) and is defined as the stress per unit elongation. The linear relationship between unit strain and normal stress (tensile or compressive stress) can be defined as follows: $E = \dfrac{\sigma}{\varepsilon}$

When force is applied to the material, the elongations occurring in the material are proportional to the stresses within elastic limits. This is called **"Hooke's Law"**. Elastic modulus is a characteristic feature of the material.

Yield Strength (σa): It is the stress value corresponding to the part where the applied tensile force remains approximately constant, but the plastic deformation increases significantly and the tensile diagram shows irregularity. $\sigma a = \dfrac{Fa}{A0}$

Tensile Strength (σç): It is defined as the highest tensile stress that a material can withstand until it breaks or breaks. This stress is the highest stress value in the tensile diagram and is found by the formula below.
$$\sigma\varsigma = \dfrac{Fmax}{A0}$$

Breaking Stress (σK): It is the stress value when the sample breaks.
$$\sigma K = \dfrac{FK}{A0}$$

Percent Elongation at Break (KU): It is defined as the highest percent plastic elongation rate occurring in the length of the tensile sample. The final length is measured by bringing together the broken parts of the sample subjected to tensile testing and the elongation in length is measured: $\Delta L = L_k - L_0$

It is found by the relation. Here, L_0 indicates the initial measurement length of the sample, and L_k indicates the length of the sample at the moment of breaking. Elongation at break is; It is determined with the help of the relation. This value shows the ductility of the material.
$$KU(\%) = \dfrac{\Delta L}{L0} x100$$

Percent Section Shrinkage (KD): It is the largest percentage contraction or shrinkage rate occurring in the cross-sectional area of the tensile sample; $KD(\%) = \dfrac{A0 - AK}{A0} x100$ It is calculated using the equation. Here, Ao indicates the initial cross-sectional area of the test sample, and AK indicates the cross-sectional area at the moment of fracture or the area of the fracture surface. To calculate EC, the expression that the volume will remain constant is used.

$$V_0 = V_K \qquad A_O.L_O = A_K.L_K \qquad A_K = A_0 \,(L_o / L_K)$$

Section narrowing is an indicator of ductility, as is elongation at break. While a significant shrinkage or necking occurs in ductile materials, brittle materials do not show shrinkage. The fracture behavior of brittle and ductile materials is shown schematically in Figure 4.

Figure 2. *(a) Fracture pattern of brittle material (b) fracture pattern of ductile material.*

1.3 EXPERIMENTAL PROCEDURES

For the tensile test, first a tensile sample in accordance with the standards is prepared from the material to be tested (Figure 2). Markings are placed on this sample. This sample, which is clamped properly and centrally between the jaws of the tensile testing machine, is pulled with an increasing load until it breaks. Meanwhile, the applied load F and the elongations (ΔL) shown by the material against it are measured by the device and video extensometer. Using the load (F) and elongation (ΔL) values obtained as a result of the experiment, the (F - ΔL) diagram is obtained. This diagram is also called a tension diagram.

1.4 INFORMATION REQUIRED IN THE EXPERIMENT REPORT

• Obtaining a stress-strain diagram separately for both force and elongation data obtained from the video extensometer.
• Calculation of elasticity modules from stress-strain diagrams.
• Calculation of yield stress, tensile strength and breaking stresses from stress-strain diagrams.
• Calculation of percent elongation at break and percent section reduction.

PART 2: HARDNESS EXPERIMENT

2.1 PURPOSE OF THE EXPERIMENT

• Measuring the hardness of materials and obtaining information about their strength.

2.2 THEOROTICAL INFORMATIONS

Hardness is defined as the resistance of materials to plastic deformation. Hardness tests are one of the very important mechanical tests that enable quick and non-destructive control of materials and manufactured parts. Hardness measurement methods commonly used in technology are methods based on measuring the size of the permanent mark obtained on the sample. In all hardness methods, at least three hardness values are measured from each sample and the average value and standard deviation are calculated.

Rockwell Hardness: Rockwell hardness test principle is given in Figure 3. While performing the Rockwell hardness test, a preload of 10 kg (F0) is first applied to the sample. This preload is applied to ensure precise contact between the sample and the tip and to eliminate gaps in the measurement system. The depth to is reached by applying the preload F0. This location is taken as the reference plane for the hardness scale. After the preload is applied, a main load (Fana) is applied to the sample for approximately 10 seconds until the load amounts given above for different hardness scales are reached. The main load values are 90 kg for the Rockwell B experiment and 140 kg for the Rockwell C experiment. After applying and removing the fan test load, which must be at least four times greater than the blow dryer force, on the sample, a permanent sinking depth tb is obtained from the reference plane. In the Rockwell device where the processes in question are carried out, the hardness value is read directly from the indicator, instead of the measured permanent tb penetration depth.
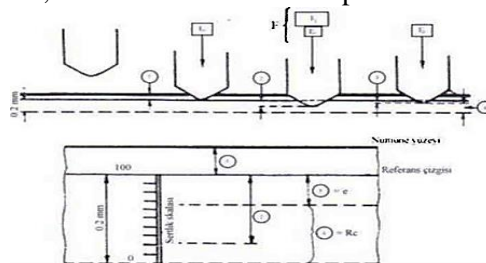

Figure 3. *Rockwell Hardness Test Procedures.*

1) The penetration depth of the tip at preload (10 kg),

2) Submersion depth of the tip at main loading (90 kg or 140 kg),

3) The penetration depth of the tip when the main load is removed (e),

4) Rockwell hardness (100-e).

Brinell Hardness: As shown in Figure 6.6, a permanent mark is created on the surface as a result of applying a certain load (F) to the surface of the material for a certain period of time with the help of a ball made of hard material of a certain diameter (D).
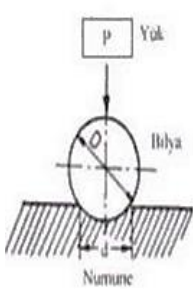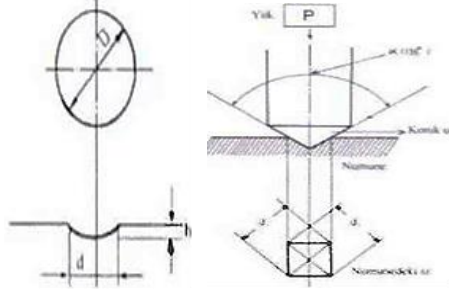

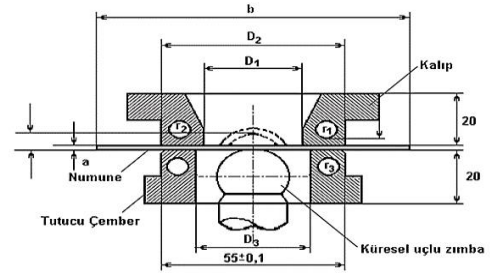**Figure 4.** *Brinell Hardness*   **Figure 5.** *Vickers Hardness*   **Figure 6.** Erichsen cupping index

The spherical surface area of the resulting trace is determined by using the measured average diameter of the trace's circumference and the ball diameter. Accordingly, Brinell hardness value:

$$\mathbf{BSD} = \frac{2F}{\Pi D \left(D - \sqrt{(D^2 - d^2)} \right)}$$

It is calculated using **F** = Applied load (kg), **D** = Ball diameter (mm), **d** = Trace diameter (mm).

Vickers Hardness: As shown in Figure 6.7, the pyramid diamond tip creates a permanent square-based mark on the material to be measured for a certain time and load. By determining the diagonal average of the symmetrical trace formed, the Vickers hardness value of the material is calculated with the help of the equation given below.

$$\mathbf{VSD} = \frac{2F \, Sin(a/2)}{d2} = \frac{1{,}8544 \, F}{d2}$$

F = Uygulanan deney yükü (kg), **d** = iz köşegenlerinin ortalaması (mm), **a** = Tepe açısı=136°.

PART 3: DEEP TENSILE TEST

3.1 PURPOSE OF THE EXPERIMENT

It is a test performed to determine the plastic deformation capability of metallic sheets and tapes. At the end of the test, the "Erichsen collapse value" is evaluated by measuring the depth in millimeters at the moment of tearing the collapsed part of the test sample with the help of a spherical tipped punch of a certain diameter.

3.2 THEORETICAL INFORMATIONS

The results of the Erichsen test are not used to standardize the materials, but rather they are examined as values that allow each material to be compared with the values of its own standard. The Erichsen test is especially applied to sheet metal and tapes used in processes such as press forming, plastering and deep drawing. The depth is the path taken from the first contact of the ball to the sheet until the moment the sheet cracks. With this test, the susceptibility of the material to plastic deformation and the macroscopic examination of the crack formed are examined. Depth depends on the sheet thickness. As the sheet thickness increases, the clamping ball is changed and more clamping force is applied. Depth values determined by curves for each sheet quality were determined. Residues such as phosphorus and sulfur that may be present in the material, as well as solidification rate, rolling method and heat treatments adversely affect the formability. The test can be performed until a crack is formed or until a certain deformation. In general, it is desired that the steel sheet does not tear. It is mostly applied on sheets used in automotive and white goods. The grain size of the material can be seen on the precipitation base. An orange-shaped surface (tattered edges) indicates coarse grain (an undesirable feature), while a shiny surface (circular crack) indicates fine grain (suitable).

"limit shrinkage ratio" with the help of the largest diameter D that can be pulled without tearing at the base of the resulting overhang called the D/d ratio. If the pressure of the compression ring is too large, the
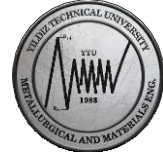
frictional forces increase and the sheet will tear prematurely; conversely, if it is too small, the sheet will fold around the periphery under the influence of compressive stresses and tear again. The forming capability is evaluated according to the magnitude of the limit shrinkage ratio. The smaller the clamping diameter, the more easily tensile cracking occurs. The indentation test apparatus is generally composed of a holding hoop and die for fixing the specimen and a ball or spherical tipped punch that forces the specimen into the die. The test apparatus makes it possible to easily and accurately determine the moment when fracture begins in the specimen. For this purpose, there is an indicator that allows to measure the greatest depth of the collapsed part at the moment when the sample starts to break. The indicator can measure the depth of the collapsed portion at 0.01 mm intervals. There are also indicators to measure the force of the specimen breaking and the force of compression of the specimen before starting the experiment. The mold, retaining ring and spherical punch on the device are made of sufficiently strong materials so that they do not change shape during the experiment, which may affect the results.

3.3 TEST SPECIMENS

The specimens to be subjected to the test must be smooth and free of folds. Normally, specimens are prepared for at least 3 tests. Before the test, the specimen should not be subjected to hot or cold treatment in order to straighten it. There should be no defects such as burrs etc. on the edges of the specimen. The specimens used in the test are sized depending on the thickness and width of the sheets or bands they represent. These dimensions are given in the table. In the TS EN ISO 20482 Metallic materials - Sheet and strips - Erichsen precipitation test standard, the diameter of each steel is specified.

Table 1. *Symbols and designations.*

Dimensions in millimetres

Symbol	Designation	Test piece and tool dimensions, and Erichsen cupping indices			
		Standard test	Tests with thicker or more narrow sheets		
a	Thickness of the test piece	$0,1 \leq a \leq 2$	$2 < a \leq 3$	$0,1 \leq a \leq 2$	$0,1 \leq a \leq 1$
b	Width or diameter of the test piece	≥ 90	≥ 90	$55 \leq b < 90$	$30 \leq b \leq 55$
d_1	Diameter of the spherical end of the punch	$20 \pm 0,05$	$20 \pm 0,05$	$15 \pm 0,02$	$8 \pm 0,02$
d_2	Bore diameter of the die	$27 \pm 0,05$	$40 \pm 0,05$	$21 \pm 0,02$	$11 \pm 0,02$
d_3	Bore diameter of the blank holder	$33 \pm 0,1$	$33 \pm 0,1$	$18 \pm 0,1$	$10 \pm 0,1$
d_4	Outside diameter of the die	$55 \pm 0,1$	$70 \pm 0,1$	$55 \pm 0,1$	$55 \pm 0,1$
d_5	Outside diameter of the blank holder	$55 \pm 0,1$	$70 \pm 0,1$	$55 \pm 0,1$	$55 \pm 0,1$
R_1	Outside corner radius of the die, outside corner radius of the blank holder	$0,75 \pm 0,1$	$1,0 \pm 0,1$	$0,75 \pm 0,1$	$0,75 \pm 0,1$
R_2	Inside corner radius of the die	$0,75 \pm 0,05$	$2,0 \pm 0,05$	$0,75 \pm 0,05$	$0,75 \pm 0,05$
h_1	Height of the inside rounded part of the die	$3,0 \pm 0,1$	$6,0 \pm 0,1$	$3,0 \pm 0,1$	$3,0 \pm 0,1$
h	Depth of the indentation during the test	—	—	—	—
IE [a]	Erichsen cupping index	IE	IE_{40}	IE_{21}	IE_{11}

[a]   The corresponding Erichsen cupping index is designated for the standard test. For thicker materials and narrower specimens of thinner materials, the d_2 dimension is added to the index.

3.4 EXPERIMENT PROCEDURES

The specimen is fixed with a precision of 0.01 mm. The specimen and spherical punch are lubricated with grease containing 23 - 28 % graphite. It is clamped between the mold and the holder ring with a load of 500 - 100 kg. When placing the specimen, make sure that the center of the collapse zone is equidistant from the edges. First, the sheet metal is compressed into the device with press load. According to the type and thickness of the steel, the speed of the plunging speed of the placed tamp is adjusted. Then, with the start of the load application, the bulge starts to form. The applied load is controlled from digital and analog indicators. It is observed that the load continues to increase for a while, but then the load value decreases. When the load starts to decrease, the load application is terminated and the device is stopped since tearing of the material is not desired. The amount of plunge, decrease in load and max. load are read from the indicators. The reason for having both analog and digital components in the device is that the variability of current and voltage does not affect the mechanical parts. Analog indicators with mechanical parts are known to be safer in case of excessive voltage fluctuations. A sample experiment data is given below. The values 8.5 mm and 18.3 kN are specimen cracking values.

Table 2. *St13 Cold Rolled Steel Sheet Test Data.*

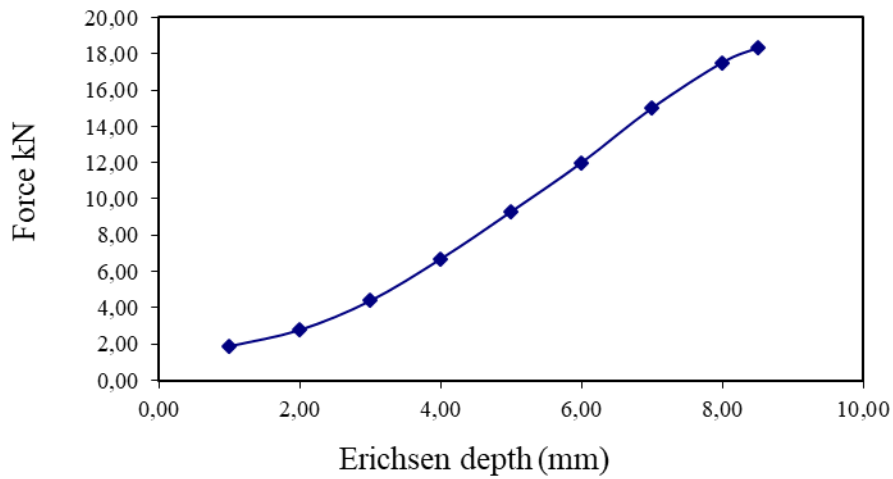| Depth (mm)	Applied Force (kN)
1	1,9
2	2,8
3	4,4
4	6,7
5	9,3
6	12
7	15
8	17,5
8,5	18,3

Figure 7. *St13 Cold Rolled Steel Sheet Test Cracking curve.*

3.5 INFORMATION REQUIRED IN THE EXPERIMENTAL REPORT

- Draw and interpret the force depth curves of the tested specimens in scale.

3.6 REFERENCES

[1] Kayalı, E.S., Ensari, C., Dikeç, F., 1996, Mechanical Testing of Metallic Materials

[2] William F. Smith 2006," Materials Science and Engineering" (Translated: Nihat G., Kınıkoğlu). Faculty of Chemistry-Metallurgy, Offset Workshop, Istanbul.

[3] TS EN ISO 6892-1 Metallic materials - Tensile test - Part 1: Test method at ambient temperature

[4] TS EN ISO 20482 Metallic materials - Sheet and strips - Erichsen precipitation test

[5] TS EN ISO 6506-1 Metallic materials - Brinell hardness test - Part 1: Test method

[6] TS EN ISO 6507-1 Metallic materials - Vickers hardness test - Part 1: Test method

[7] TS EN ISO 6508-1 Metallic materials - Rockwell hardness test - Part 1: Test method

EXPERIMENT 2: PRECIPITATION HARDENING

1. PURPOSE OF THE EXPERIMENT

- The primary purpose of the precipitation hardening experiment is <u>to examine the effect of the applied process on the mechanical properties (strength, hardness, etc.)</u> of materials that can respond to heat treatment (such as 2xxx, 6xxx, and 7xxx series aluminum alloys).

- Improving the mechanical properties of the material with thermal methods <u>without changing the chemical composition</u>

2. THEORETICAL INFORMATION

The mechanical properties of materials are largely dependent on their internal structure. Since the internal structure is related to the chemical composition and the mechanical or heat treatments applied to the material, it can be said that the mechanical properties of the materials also depend on these factors. In this context, <u>strength</u> is one of the most important mechanical properties of a material and is expressed as "resistance to plastic deformation". Plastic deformation of metals is mainly caused by the progression of linear defects called <u>dislocations</u> in the crystal. Therefore, mechanical properties such as strength, hardness, and ductility are explained by both the density of the dislocations in the internal structures of metals and their interactions with other components and defects. Any factor that will complicate or prevent the movement of dislocations in the internal structure of metals will lead to an increase in the strength of the material. Conversely, any factor that will facilitate dislocation movements will enable plastic deformation to occur more easily.

There are various methods used to strengthen metallic materials. The main ones can be classified as; Strain hardening, Alloying, Grain size reduction, Martensitic transformation hardening, <u>Precipitation hardening,</u> etc. With the development of technology and due to its technical features, aluminum, which is one of the youngest members of the global metal world, is widely used in many areas of industry. In practice, aluminum, which has a very high strength-to-weight ratio and is quite light compared to steel; has become especially attractive for industries such as automotive, and aerospace industries, since its mechanical properties can be increased to a level comparable to steel when it is doped by the addition of alloying elements [1].

Heat treatment generally includes heating and cooling processes applied to metallic materials to change their mechanical properties. In this context, **precipitation hardening/aging heat treatment** can be applied to suitable aluminum alloys.

Aging can only occur in alloys with a solvus curve in the equilibrium diagram, and solid solution compositions are limited only by the solvus curve. Elements such as Cu, Zn, Mg, and Si added into Al alloys make this alloy applicable for precipitation hardening with the intermetallic structures they form in the primary phase [2]. Therefore, precipitation hardening heat treatment can be applied to 2xxx (Al-Cu), 6xxx (Al-Mg-Si), and 7xxx (Al-Zn-Mg) series aluminum alloys. The phase diagram of the 2xxx series Al alloy, which can be applied to precipitation hardening heat treatment, is given in Figure 1. Thanks to the precipitation hardening process, it is possible to develop light and high strength-to-weight Al alloys suitable for use in the aerospace industry.
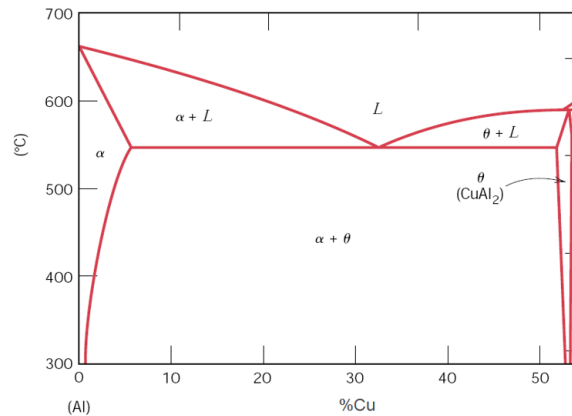
Figure 1. Phase diagram of 2xxx series Al alloy that can be precipitation hardening heat treatable.

The first precipitation hardening application for an increase in strength and hardness of Al alloys was examined by Alfred Wilm in the early 20th century (1906). Alfred Wilm, in his studies on aluminum alloys, observed that duraluminum gained hardness because of sudden cooling from high temperature (quenching) and waiting at room temperature, just like steel. The increase in hardness of the aluminum alloy known as duraluminium (Al-4.4%Cu-1.5% Mg-0.5%Mn) because of quenching and waiting at room temperature is called natural aging. Waiting for a certain period at a temperature between 100°C-300°C after quenching is called artificial aging. It has been revealed in later studies that the aging time is shortened by increasing the aging temperature. However, if the aging temperature is too high or the aging time is too long, in this case, the so-called over-aging phenomena occur and a decrease in material strength is observed again [3]. On the other hand, the type, distribution, amount, average diameter, and number of the precipitated second phases affect the strength of the material.

The precipitation hardening heat treatment is conducted in three stages:
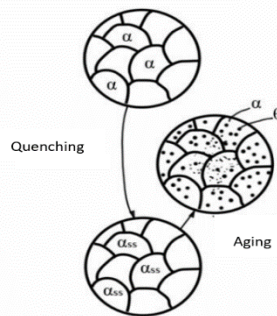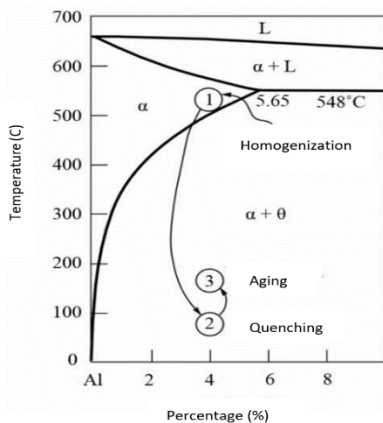
1. Solution Treating: High-temperature annealing (Homogenization process) to homogenize the alloy.

2. Quenching: Obtaining supersaturated structure with sudden cooling in a water environment (α_{ss})

3. Aging (Natural/Artificial): Aging for a certain period at a temperature below the homogenization temperature (100-300°C)

**Figure 2.** Precipitation hardening process steps and the changes in microstructure [4]

The precipitation hardening process steps and changes in the microstructure are given in Figure 2 [4].

3. TOOLS, DEVICES and MATERIALS

- Samples of 6xxx series aluminum alloy,
- Oven that can reach an elevated temperature for solution treating,
- Sudden cooling (Quenching) environment,
- An oven that can be heated to 300°C for artificial aging,
- Brinell hardness device.
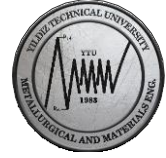
4. EXPERIMENTAL PROCEDURES

As the test sample, 6xxx series Al alloy with a thickness of at least two mm and containing Al-Mg-Si was preferred. Within the scope of the experiment, four samples are used to determine the effect of aging time on the hardness of the material.

In the first stage of the experiment, all samples are placed in the oven at 530-550°C for approximately 30 minutes to apply "Homogenization annealing". After the period specified, as the second stage, the samples are taken out of the furnace as quickly as possible and instantly cooled in a water environment to ensure "sudden cooling".

One of the samples is separated so that the hardness can be measured without applying artificial aging, and the other three samples are subjected to artificial aging for specified periods in an oven at approximately 200°C. For measuring the hardness, the samples are taken out of the oven at the end of the applied aging period and cooled rapidly. Hardness measurement should be done quickly, as the time spent outside the oven will affect the result. Hardness measurements are carried out by using a Brinell hardness measuring device.

5. RESULTS and DISCUSSION

The formula to be used in the determination of the Brinell hardness values is given in Equation 1.

$$HB = \frac{F}{2 \times \pi \times D \times (D - \sqrt{D^2 - d^2})} \tag{1}$$

F: Force (N,kg), D: Ball diameter (mm), d: Mark diameter (mm)
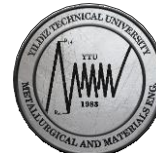
To make comparisons by using the data obtained because of the experiment, a hardness-aging time graph will be created.

6. INFORMATION REQUIRED IN THE EXPERIMENT REPORT

- **Cover Page:** In accordance with the format; Emblem, Course Information, Supervisor of the Experiment, Student Name-Surname/Student Number, and Group Number

- **Theoretical Information:** An original summary of the knowledge conveyed on the relevant subject during the experiment, prepared by the student.

- **Experimental Studies:** Materials and equipment used in the experiment; The procedure steps explained in accordance with the application conditions and the order of the experiment (with cause and results); Brinell hardness calculations (with units)

- **Evaluation:** Drawing a Brinell Hardness-Time graph by using Excel graphics, researching the data in the existing literature, comparing it with the results obtained within the scope of the experiment, and interpretation by the student.

7. REFERENCES

[1]   GÜVEN, Ş. ve DELİKANLI, Y., (2012). "AA 2024 Alüminyum Alaşımında Çökelme Sertleşmesinin Mekanik Özelliklere Etkisi", Teknik Bilimler Dergisi, 2: 13-20.

[2]   YAMAN, M.B. KOCAMAN, E. ve Barış, A., "Al7075 Alaşımına İlave Edilen Al-5Ti-1B Tane İncelticinin Yaşlanma, Mikroyapı, Sertlik ve Korozif Özellikleri Üzerindeki Etkisi", Gazi University Journal of Science Part C: Design and Technology, 10: 870-883.

[3]   YAŞAR, A.C. ESER, A.A. ÖZCAN, A. ve ACARER, M., "ALÜMİNYUM DÖVME VE EKSTRÜZYON ALAŞIMLARINDA AŞIRI YAŞLANDIRMANIN MİKROYAPI ve MEKANİK ÖZELLİKLERE ETKİSİ".

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EXPERIMENT 3: CORROSION EXPERIMENT

PART 1: CORROSION OF ZINC IN ACIDIC SOLUTION

1.1 PURPOSE OF EXPERIMENT

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

1.2 THEOROTICAL INFORMATION

Corrosion is the occurrence of undesirable changes in the physical, chemical, and mechanical properties of materials in general, metals and alloys in particular, because of the environment they are in. Metals are found in their most stable form as ores in the earth's crust. They are normally extracted from their ores via certain processes that require energy. Metals are unstable in their pure metallic state because they are believed to be in the excited state. As a result, when metals are exposed to the environment in various forms, the exposed metal surface begins to degrade. Corroded metal is more thermodynamically stable than pure metal, but it loses important qualities, including malleability, ductility, hardness, conductivity etc. 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.
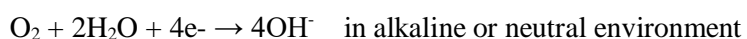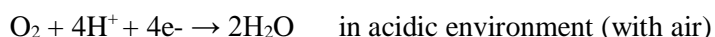
When different metals and alloys come into contact with each other in the same environment, the more active one is corroded by acting as an anode, while the other metal is protected from corrosion by acting as a cathode. On the other hand, two different metals do not necessarily have to be present in 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:

$Me0 \rightarrow Me^{+2} + 2e-$

On cathode:

$2H+ + 2e- \rightarrow H_2$ in acidic environment

$O_2 + 4H^+ + 4e- \rightarrow 2H_2O$ in acidic environment (with air)

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

$Me^{+2} + 2e- \rightarrow Me0$ in any environment

Corrosion occurs at the anode sites. On the other hand, cathodic reactions take place at the cathode, and degradation does not occur in these regions of the metal. 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
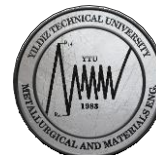
of gas released during the test. In determining the corrosion rate, the method that will give the most accurate result should be selected.

The corrosion rate can be expressed in various units. The most commonly used ones are; $mg/dm^2.day$ (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.

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

H: corrosion rate, **K**: constant for the desired corrosion rate unit ($3.45x10^6$ for 'mpy'), **G**: weight loss (g) **A**: surface area exposed to the solution (cm^2), **d**: metal density (g/cm^3)   **t**: duration of the 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'.

1.3 TOOL, DEVICES and MATERIALS

- Zinc, beaker, glass funnel, 0.1 M HCl solution, burette, pipette pump, drying machine, scales, polishing paper.

1.4 EXPERIMENTAL PROCEDURES

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 waterproof 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.
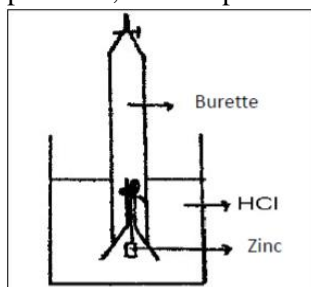

Figure 1. Experimental set-up

1.4 INFORMATION REQUIRED IN THE EXPERIMENT REPORT

- Write cathodic and anodic reactions. **(5 points)**

- Calculate the total corrosion rate (mpy) using the method of calculating the mass loss. **(10 points)**

- Calculate the total corrosion rate (mpy) using the method of 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 gas volume readings in the burette during experiments. **(20 points)**

- Compare the corrosion rates calculated using both the methods of calculating the mass loss of the samples and determining the amount of the evolved gas during the test. Is the corrosion rate determined by weight loss the same as the rate of corrosion determined by the loss of hydrogen gas? If not, indicate the reasons. **(15 points)**

PART 2: CORROSION OF LEAD IN ACIDIC SOLUTION

2.1 PURPOSE OF EXPERIMENT

- Measuring the corrosion rate of lead in acidic solution by Tafel Extrapolation Method.

2.2 THEOROTICAL 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 (Ecorr)' is formed on the electrode surface because of the balance of two different reactions, one anodic and the other cathodic. Generally, Tafel kinetics are an accurate explanation of corrosion kinetics for conditions under which mass transport limitations are not considered, because corrosion conditions usually are removed from the reversible potentials for all the reactions.

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: Tafel extrapolation method and linear polarization method.

Tafel extrapolation method:

Tafel extrapolation is one of the polarization methods widely utilized to measure corrosion rates, a faster experimental technique compared with the classical weight-loss estimation [36]. It is known that the corrosion rates obtained using Tafel extrapolation of polarization curves are not usually the same as those measured by weight loss. 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'.
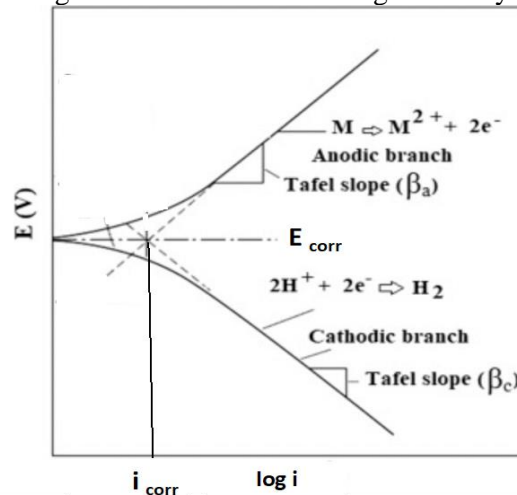

Figure 2. Tafel region of the polarization curve

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

$$Corrosion\ Rate = K\ x\ \frac{(i_{corr}\ x\ EW)}{d}$$

K = constant number, 3.27×10^{-3} mm.g/μA.cm.year, **i_corr** = current density (A/cm^2), **EW** = equivalent weight of the sample, **d** = density of the sample, g/cm^3

2.3 TOOL, DEVICES and MATERIALS

- Potentiostat, lead sample, 1 M H_2SO_4 solution, 5-necked cell, lead counter electrodes, saturated calomel reference electrode, crocodile cable, dryer machine, glue gun, silicone.

2.4 EXPERIMENTAL PROCEDURES

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 for an active surface area of 1 cm^2. 1 M H_2SO_4 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.

2.5 INFORMATION REQUIRED IN THE EXPERIMENT REPORT

- Write the anodic and cathodic reactions that took place in the experiment for the lead sample in H_2SO_4 solution. **(5 points)**

- Calculate the corrosion rate of the sample in mm/year with the help of the i_{corr} value obtained from the Tafel curve. **(15 points)**

- 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. **(10 points)**

- Select 2 methods of protection from corrosion and explain these methods. **(15 points)**

- Please support your report with theoric information on necessary parts and show references correctly. **(5 points)**

! Bringing your calculators with you is recommended !

2.6 REFERENCES:

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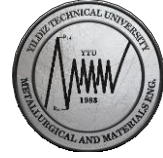
EXPERIMENT 4: PRODUCTION OF THERMOSET POLYMERS

POLYMERS: UNSATURATED POLYESTER RESINS (THERMOSETS)

1. PURPOSE OF THE EXPERIMENT

- To observe the effect of reaction components on the cross-linking (hardening, curing) rate in thermosetting polymers. Graphically drawing and interpreting the results obtained from the experiment.

2. THEOROTICAL INFORMATIONS

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

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

The definition of unsaturated polyester is used for polyester polymers with double bonds (unsaturation) in the polymer chains. Such a polyester resin can be synthesized through a condensation reaction between glycol (an alcohol with two –OH groups) and an equivalent amount of an anhydride (or instead a diacid with two –COOH groups) containing a double carbon-carbon bond (Figure 1). Certain properties in commercial resins can be obtained with different diol and diacid blends. During the condensation reaction, the double bond of the anhydride does not react and remains on the linear polyester chains. The unsaturated polyester pre-polymer obtained in this stage exhibits thermoplastic properties that can be re-hardened when cooled while being softened and fluidized when heated.
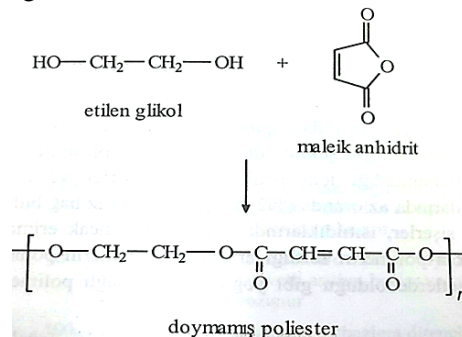

Figure 1. *Synthesis of unsaturated polyester.*

In the second phase; in the presence of a suitable initiator the unsaturated polyester is heated to the decomposition temperature of the initiator with a vinyl monomer ($CH_2 = CHR$) such as a resolvent styrene, the double bonds in the linear polyester chains are opened and they cross-link (curing, hardening) with styrene molecules via radicalic polymerization mechanism. In the end of this process, the linear and unsaturated polyester chains are copolymerized with a monomer such as styrene into a cross-linked

17

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.
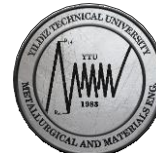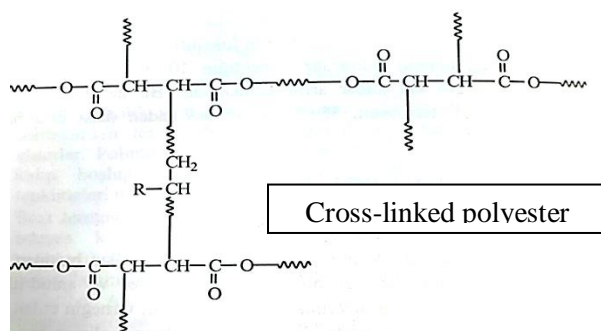

Figure 2. *Vinyl monomer-cured cross-linked polyester.*

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=HiEzlDLlcu4
- 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.

3. TOOLS, DEVICES AND MATERIALS

Resin: Unsaturated polyester / styrene mixture

Initiator: Methyl ethyl ketone (MEK) peroxide

Accelerator: Cobalt naphthenate

Other materials: Plastic cups, wood stick, nitrile gloves, chronometer and plastic pipette.

4. EXPERIMENTAL PROCEDURES

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.
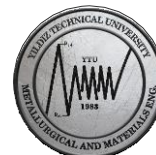
2) Obtaining Results: After each student has recorded their own gel time, they will collect the relevant data by taking the gel times of other students.

5. INFORMATION REQUIRED IN THE EXPERIMENT REPORT

- Give general information about the theoretical part that was explained to you before the experiment. (10 points)

- Describe the procedure of the experiment in detail. (20 Points)

- What is the gelation time you determined in the first step of the experiment? Discuss the effects of reaction conditions and environmental factors on the gelation time. (10 points)

- Plot the gelation time curve against the changing accelerator concentration determined in step 1 and interpret the behaviour of the curve. (25 Points)

- Plot the gelation time curve against the changing initiator concentration determined in step 1 and interpret the behaviour of the curve. (25 Points)

- Describe your observations at each stage of the unsaturated polyester resin gelation experiment, the results of the experiment, and what you have learned from the experiment. (10 Points)

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EXPERIMENT 5: REDUCTION ELECTROLYSIS AND HYDROMETALLURGY

1. PURPOSE 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 efficiency.

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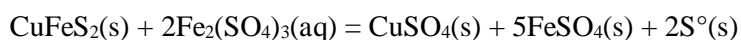
2. HYDROMETALLURGY THEORETICAL INFORMATION

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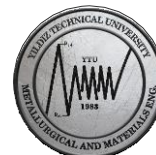
Chalcopyrite is the most common copper ore so hydrometallurgical researches and efforts are focused on this kind ores. Reactions of chalcopyrite mineral in the sulphuric acid leach solution are given below.

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

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

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

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

Factors Affecting Leaching: Most hydrometallurgical processes involve heterogeneous reactions (the

type of reaction between multiple phases). The rate of these reactions depends primarily on the hydrodynamics of the leaching system (such as mixing and diffusion) and the chemical interactions of the components present in the system. Clearly, leaching of any ore in an aqueous environment is influenced by the following factors: *Grain size of the ore, Composition of the ore, Composition and concentration of the solvent, Contact time of the ore with the solvent, 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 Zn2+ ions by anodic half-cell reaction: $Zn_0 \rightarrow Zn^{2+} + 2e-$

2.   Formation of metallic copper by cathodic half-cell reaction: $Cu^{2+} + 2e- \rightarrow Cu_0$

3.   Total cell reaction: $Cu^{2+}(aq) + Zn_0(s) \rightarrow Cu_0(s) + Zn^{2+}(aq)$

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

Anodic reaction: $Zn_0 \rightarrow Zn^{+2} + 2e-$

Cathodic reaction: $Cu_0 \rightarrow Cu^{+2} + 2e-$

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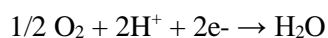
Cementation Chemistry: If an iron component is immersed in an aqueous solution containing copper ions metallic copper tends to precipitate, while iron tends to go through the solution. Electrochemical potential is the driving force of this reaction. This potential is calculated with Nernst equation given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

$Fe_0 + Cu^{2+} = Cu^0 + Fe^{2+}$ (1)

$E = E_0 + (RT / nF) \ x \ ln(a_{Me})$ (2)

In this equation, E = Real potential (V), E_0 = Standard potential (V), R = Gas constant, T = Temperature (K), n = Oxidation level, F = Faraday constant (C.mol^{-1}), a = Activity.

If the Nernst equation would apply to the copper iron couple; $E_{Cu} = E_{Fe}$ (3)

$Eo_{Cu} + (RT/nF) \ x \ ln \ (a_{Cu2+}) = Eo_{Fe} + (RT/nF) \ x \ ln \ (a_{Fe2+})$ (4)

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

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

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

This result theoretically means that there is only 1 copper ion (Cu^{2+}) per 1027 iron ions (Fe^{2+}) in solution after cementation. This very large ratio means that the reaction (1) completely moves to right side. According to reaction (1) 1 molar iron (55.85 g) cementite 1 molar copper (63.54 g). This value is determined as 1 kg iron per 1 kg of copper. In industrial applications 1.5-2.5 kg iron is required due to the following side reactions.

$Fe_0 + 2Fe^{3+} = 3Fe^{2+}$ (8)

$Fe_0 + 2H^+ = Fe^{2+} + H_2O$ (9)

The oxygen of the air is directly oxidized +2 valence iron causing iron consumption. The selection of metals in the cementation process is made according to the EMF series.
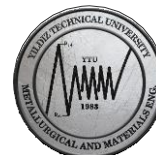
Electrode Reaction	Potential, V° (V)
$Au^{3+} + 3e^{-} \longrightarrow Au$	+1.420
$O_2 + 4H^{+} + 4e^{-} \longrightarrow 2H_2O$	+1.229
$Pt^{2+} + 2e^{-} \longrightarrow Pt$	~ +1.2
$Ag^{+} + e^{-} \longrightarrow Ag$	+0.800
$Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$	+0.771
$O_2 + 2H_2O + 4e^{-} \longrightarrow 4(OH^{-})$	+0.401
$Cu^{2+} + 2e^{-} \longrightarrow Cu$	+0.340
$2H^{+} + 2e^{-} \longrightarrow H_2$	0.000
$Pb^{2+} + 2e^{-} \longrightarrow Pb$	−0.126
$Sn^{2+} + 2e^{-} \longrightarrow Sn$	−0.136
$Ni^{2+} + 2e^{-} \longrightarrow Ni$	−0.250
$Co^{2+} + 2e^{-} \longrightarrow Co$	−0.277
$Cd^{2+} + 2e^{-} \longrightarrow Cd$	−0.403
$Fe^{2+} + 2e^{-} \longrightarrow Fe$	−0.440
$Cr^{3+} + 3e^{-} \longrightarrow Cr$	−0.744
$Zn^{2+} + 2e^{-} \longrightarrow Zn$	−0.763
$Al^{3+} + 3e^{-} \longrightarrow Al$	−1.662
$Mg^{2+} + 2e^{-} \longrightarrow Mg$	−2.363
$Na^{+} + e^{-} \longrightarrow Na$	−2.714
$K^{+} + e^{-} \longrightarrow K$	−2.924

3. TOOLS, DEVICES, AND MATERIALS

- Chalcopyrite ore, Copper sulphate, sulphuric acid, purified water, precise scale, heated magnetic mixer, mixed water bath, pipette, washing bottle, beaker, funnel, filter paper.

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

4. EXPERIMENTAL PROCEDURES

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. The amount of dissolved in solution is analyzed by Atomic Absorption Spectrometer. The reason for the high or low dissolution efficiency value is discussed. 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. Copper recovery rate is calculated for each test group. All the results obtained are interpreted.

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.

- Calculate precipitated copper efficiency using the results of Cu analysis after precipitation and filtration of the precipitated parts obtained in the test results with CuSO4 solution containing 5 g / 200 ml Cu with Fe and Zn powder.

- Explain the relationship between precipitation efficiencies and pH values.

- Which sementator provided higher efficiency? (Zn or Fe) Explain in detail.

- 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

5. WHAT IS ELECTROMETALLURGY?

Electrometallurgy is the recovery and purification of metals through electrolytic processes by using electrical energy. Electrometallurgy makes use of electrothermal and electrochemical processes. Electroth ermal processes are used toextract metals from ores and concentrates and to produce and refin e ferrous and nonferrous metals and alloys based on themetals extracted. In such processes, el ectric energy is used as a source of heat. Electrometallurgy deals with technical aspect of metal electrodeposition. The electrometallurgical processes can be categorized into four main groups: *Electrowinning, Electrorefining, Electroplating, Electroforming.*
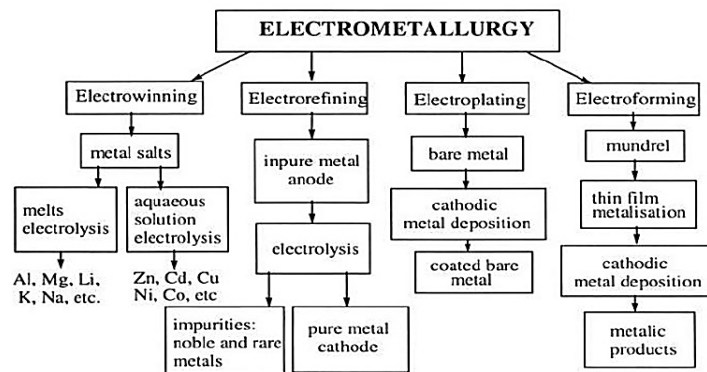
Figure 1. *Schematic illustration of electrometallurgical processes.*

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

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

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

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

Electroless metal deposition and anodic oxidation of metals can also be include in the field of electrometallurgy. Empirically is known what type of deposit can be obtained under specific conditions, however how and why this can be achieved still remains a mystery in some cases.

BASIC FACTS

Electrodes and electrochemical reactions, cell and circuit

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

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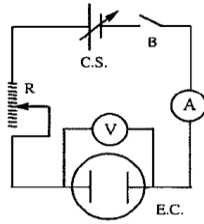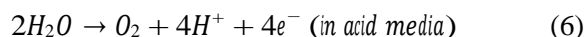

Figure 2. An electrochemical circuit. **C.S.-**current source, **R** -ohmic resistance, **V** - voltmeter, **A**-ampermeter, **E.C**- electrochemical cell, **B** - circuit breaker.

The electrochemical circuit consists of a current source, metallic connecting wires, an electrochemical cell, ohmic resistance, current and voltage measuring instruments and a circuit breaker. In technical practice more complicated circuits are used, but in principle all of them are the 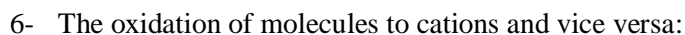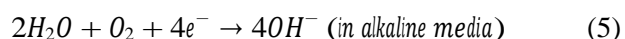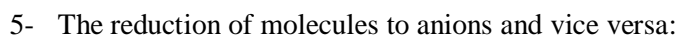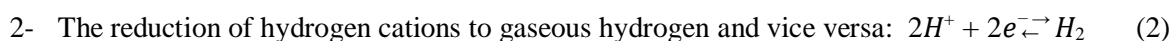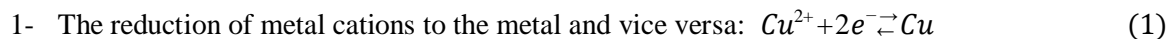same as the one shown in Fig. 2. Obviously, a steady current flow in the circuit from Fig. 2. can only be maintained if there is a change of charge carrier at the metal-electrolyte interface by a chemical transformation involving the transfer of electrons across the interface, i.e., by an electrochemical reaction. It constitutes the bridge between the current of electrons in the metallic part of the electrochemical circuit and the current of ions in the electrolytic part of the circuit.
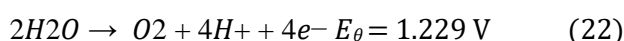
The electrochemical double layer and possible electrochemical reactions

If the metal ions in the solution are the same as in the electrode metal lattice, or if the same substance is present in the electrolyte in two oxidation states, an electron transfer reaction can occur at the metal-electrolyte interface and lead to the development of a potential difference. Such an interface behaves like an electrical circuit consisting of a resistor and a capacitor in parallel. The electron transfer takes place until a dynamic equilibrium is reached. In the case of metal electrodes, depending on the system, this process begins with either the deposition of ions from solution onto the metal electrode or with the dissolution of the metal electrode. In equilibrium the electrode is more positive than the solution in the first case and more negative in the second one. A number of electrochemical reactions are possible at such an interface, as for example:
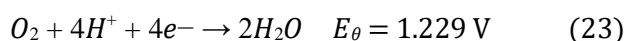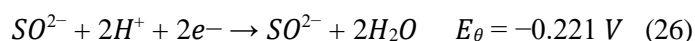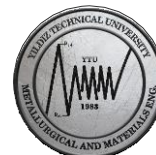
1- The reduction of metal cations to the metal and vice versa: $Cu^{2+} + 2e^- \rightleftarrows Cu$ (1)

2- The reduction of hydrogen cations to gaseous hydrogen and vice versa: $2H^+ + 2e^- \rightleftarrows H_2$ (2)

3- The decrease of the oxidation state of the cations and vice versa: $Fe^{3+} + e^- \rightleftarrows Fe^{2+}$ (3)

4- The reduction of anions to metal and vice versa: $[Cd(CN)_4]^{2-} + 2e^- \rightleftarrows Cd + 4CN^-$ (4)

5- The reduction of molecules to anions and vice versa:

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

6- The oxidation of molecules to cations and vice versa:

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

A cell with an insoluble anode

In the driven cell: $(-)Cu|CuSO4, H2SO4, H2O|Au(+)$ the following reactions on the anode

(Au) are possible:

$2SO^{2-} \rightarrow S_2O^{2-} + 2e-$ $E_\theta = 2.010\ V$ (20)

$Au \rightarrow Au3+ + 3e-$ $E_\theta = 1.498\ V$ (21)

$2H2O \rightarrow O2 + 4H+ + 4e-$ $E_\theta = 1.229\ V$ (22)

and on the cathode (Cu)

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E_\theta = 1.229\ V$ (23)

$Cu^{2+} + 2e- \rightarrow Cu$ $\qquad\qquad E_\theta = 0.337$ V (24)

$2H+ + 2e- \rightarrow H_2$ $\qquad\qquad E_\theta = 0.000\ V$ (25)

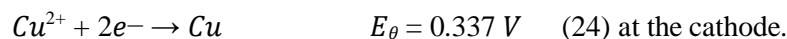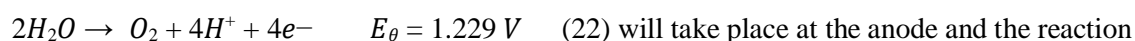$SO^{2-} + 2H^+ + 2e- \rightarrow SO^{2-} + 2H_2O$ $\quad E_\theta = -0.221\ V$ (26)

According to the rule derived in the conclusion from section 2.3.1, on the anode the oxygen evolution reaction will occur, and on the cathode copper ions will be reduced to the metal phase, because the most positive catodic reaction can be neglected due to the low oxygen concentration in the electrolyte solution. Hence the reaction:
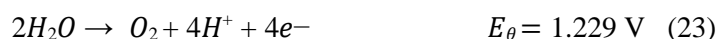
$2H_2O \rightarrow\ O_2 + 4H^+ + 4e-$ $\qquad E_\theta = 1.229\ V$ (22) will take place at the anode and the reaction

$Cu^{2+} + 2e- \rightarrow Cu$ $\qquad\qquad E_\theta = 0.337\ V$ (24) at the cathode.

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

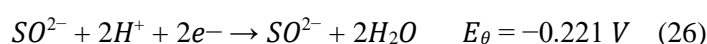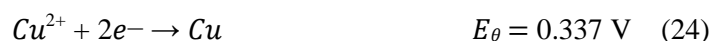$2Cu^{2+} + 2H_2O \rightarrow 2Cu + O_2 + 4H^+$ $\qquad\qquad$ (25)
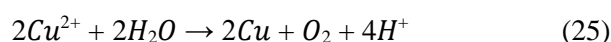
It follows from the Eq. 25 that in a cell with an insoluble anode the concentration of depositing ions decreases and the hydrogen ion concentration increases during electrolysis. The mechanism of the extraction of metals from ionic solutions and the essence of the electrowinning process are well explained by Eq. 25.
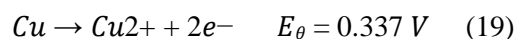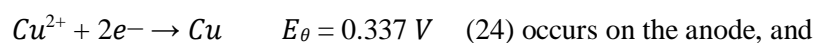
A cell with a soluble anode

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

$2SO^{2-} \rightarrow S_2O^{2-} + 2e-$ $\qquad\qquad E_\theta = 2.010\ V$ (20)

$2H_2O \rightarrow\ O_2 + 4H^+ + 4e-$ $\qquad\qquad E_\theta = 1.229$ V (23)

$Cu2+ + 2e- \rightarrow Cu$ $\qquad\qquad E_\theta = 0.337$ V (24)

and on the cathode (Au):

$O_2 + 4H^+ + 4e- \rightarrow 2H_2O$ $\qquad\qquad E_\theta = 1.229$ V (23)

$Cu^{2+} + 2e- \rightarrow Cu$ $\qquad\qquad E_\theta = 0.337$ V (24)

$2H+ + 2e- \rightarrow H2$ $\qquad\qquad E_\theta = 0.000\ V$ (25)

$SO^{2-} + 2H^+ + 2e- \rightarrow SO^{2-} + 2H_2O$ $\quad E_\theta = -0.221\ V$ (26)

Hence, the reaction

$Cu^{2+} + 2e- \rightarrow Cu$ $\qquad E_\theta = 0.337\ V$ (24) occurs on the anode, and

$Cu \rightarrow Cu2+ + 2e-$ $\qquad E_\theta = 0.337\ V$ (19)

at the cathode, and so the composition of the electrolyte solution remains constant if the anode is made of pure copper and oxygen is removed from the solution. The lowest cell voltage at which electrolysis can start in this cell is zero. It is obvious that electrorefining processes are based on electrolysis in cells with soluble anodes.

Current efficiency

Metal deposition can be accompanied by any other cathodic reaction, most frequently hydrogen evolution. This leads to the situation in which metal is deposited but metal deposition uses only a part, I Me of the total current, I, through the cell. The current efficiency $\eta =\ IMe_I$ (27)

indicates which part of the total current is used for the deposition of metals. It is a very important parameter of an electrodeposition process.

Faraday's law: Faraday's law relates the quantity of electricity passed through the cell and the quantity of chemical substances which react on the electrodes. It states that the mass of metal, m, electrodeposited on the cathode is given by $m = ItM\ \eta$ (28) nF_I

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

6. TOOLS, DEVICES AND MATERIALS

Apparatus: Eye protection, Beaker (250 cm^3), Stainless steel plate cathodes and one hard lead plate anode electrodes (about 5 mm diameter), 2 Retort stand and clamp to hold electrodes, DC power supply (6 volt),Leads and crocodile clips 4.

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

7. EXPERIMENTAL PROCEDURES

Electrolysis is the chemical process of using an electrical current to stimulate non- spontaneous reactions. A non-spontaneous reaction is one that needs energy to work while it proceeds. In other words, the process would not happen on its own, as it goes in an unfavourable, or a reversed, direction. Important uses include its role in separating metals from a natural source, such as our friend the copper ore. Other useful benefits for electrolysis include the purification of metals and decomposition of compounds like water. The site where electrolysis occurs is in an electrolytic cell, which is a type of electrochemical cell that drives an electrical current using a non-spontaneous reaction. So, not like a cell in your body, but a container. Thus, these cells must have an energy source to drive the reaction in the reverse or opposite direction, like a battery. Be careful not to confuse an electrolytic cell with electrolysis. Always remember that the electrolysis process is performed using an electrolytic cell.

How Does Electrolysis Work?

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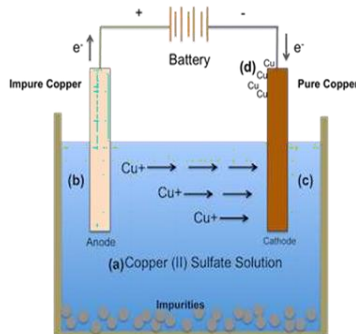

Figure 5. *Schematic representation of copper (II) sulphate solution electrolysis cell.*

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

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

Two experiments are performed in which all parameters except the current intensity are kept constant

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

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

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EXPERIMENT 6: CERAMIC EXPERIMENT

1. PURPOSE OF 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. THEOROTICAL INFORMATION

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 auxilary agents such as binders, defflocculants 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 contant 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 thixotrophy. Viscosity is the value of the fluidity of a material, fluidity and viscosity has an inverse ratio between them. Thixotrophy 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 thixotrophy property. For the rheological study of a ceramic slurry, terms like flocculation, defloculation 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 thixotrophy, it is also as important as viscosity. If the thixotrophy is too high, drying time of the product will be long and if the thixotrophy is too low, this will cause the product to become fragile.

2.2 Flocculation, Deflocculation, Defloculant

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 seperate 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 viscostiy. 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.

2.3 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 alkiline 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 meechanisms. Mechanisms does not depend on the nature of the deflocculant, it can either be organic or inorganic.

3. TOOL, DEVICES, and MATERIALS

- Mill, Viscometer, Stirrer, Pyknometer, Sieve (90 μm) Drying Oven, Weighing Instrument

4. EXPERIMENTAL PROCEDURE

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 4 – 6 Poise (necessary value for floor tiles), deflocculant addition to the slurry is started. To obtain the thixotrophy, 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 thixotrophy. After the stabilization of the viscosity was achieved between 4 – 6 Poise, addition of the deflocculant is stopped. When the slurry reaches it's 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.
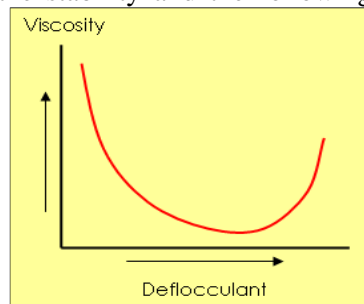

Figure 1. Viscosity-Added deflocculant diagram

5. RESULTS

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

6. INFORMATION REQUIRED IN THE EXPERIMENT REPORT

- Purpose of the experiment and brief theoretical information about the experiment

- The implementation of the experiment will be explained in an original language, in the order of the experiment.

- The theoretical and practical usage percentages of the materials used in the experiment will be tabulated. (EXCEL)

The experiment will not exceed 2 pages and will be written by hand. It is mandatory to create a cover for the test report.

7. REFERENCES

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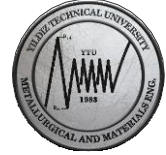
EXPERIMENT 7: OPTICAL PROPERTIES OF MATERIALS

1. PURPOSE OF EXPERIMENT

- measure the transmittance of ultraviolet and visible radiation by a set of standards optical materials.

- observe the transmittance of visible and ultraviolet radiation by optical materials and see the amount of radiation blocked out by these samples.

2. THEORETICAL INFORMATION

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.
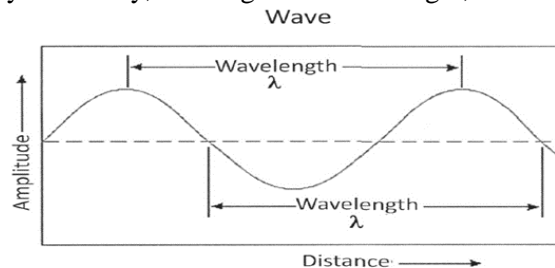

Fig. 1: *The description of wavelength*

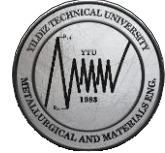Wavelength and frequency are related by the speed of light (c = 2.998 x 1010 cm/sec).

$$c = \lambda \nu$$

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 x 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 x 10^{-5} cm) to about 400 nm (4.0 x 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.
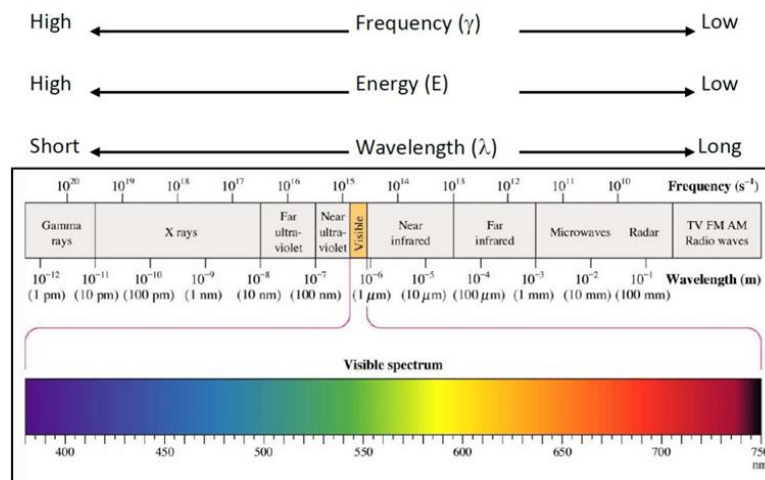

Fig. 2: *Electromagnetic Spectrum*

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, diffracted, 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.

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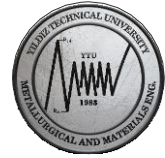
The absorption spectrum is characterized by the wavelength of maximum absorption (λmax) at which the absorbance is the greatest (see Fig. 3 below. The value of λmax is important for several reasons. It is used in order to obtain the highest sensitivity and to minimize deviations from Beer's Law (see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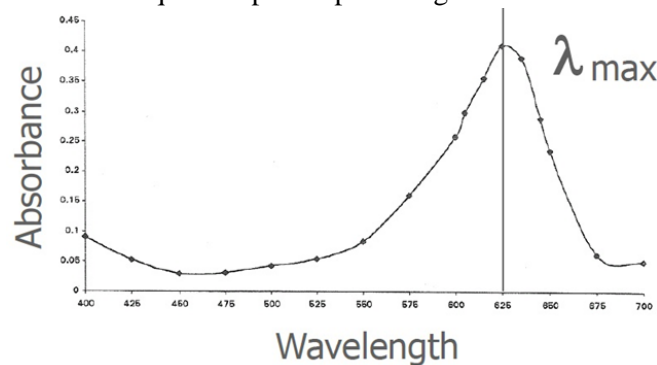

Fig. 3: *The example of an absorption spectrum*

The Beer-Lambert Law: The Beer-Lambert Law is a set of mathematical equations that demonstrate the connection between the properties of a material and the absorption of light. These equations are used to calculate two fundamental variables, namely transmittance (T), percent transmittance (%T), and absorbance (A).

$$T = I / I_0$$

$$\%T = I / I_0 *100$$

$$A = -\log T = -\log_{10}(I / I_0)$$

Looking at these equations, it is evident that there is a logarithmic relationship between the transmittance and absorption properties of a substance.

3. TOOLS, DEVICES and MATERIALS

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

4. EXPERIMENTAL PROCEDURE

%Transmittance Measurement:

1- The device is turned on, and the lamps are allowed to warm up.

2- Measurement parameters (wavelength range, sensitivity, lamps, etc.) are selected.

3- A baseline is taken for the specified measurement conditions before any sample is placed in the device.

4- The sample to be measured is placed in the sample holder.

5- Measurement is performed using the same measurement parameters.

6- The obtained spectrum is examined.

### 5. POST-LAB QUESTIONS

1- Please answer the following questions with one sentence each **(20 points):**

a. Which type of ultraviolet radiation has the highest energy, and what is its wavelength range?

b. Which type of ultraviolet radiation is most harmful to our eyes?

c. What types of radiation should sunglasses block?

d. A absorption spectrum reaches its maximum point at 540 nm. What does this mean?

e. A transmission spectrum forms a peak at 500 nm, with 80% intensity between 480-524 nm. What does this mean?
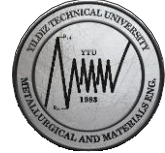
2- Explain the measurement process using a spectrophotometer step by step, starting from the sample preparation stage. **(10 points)**

3- Draw the graphs of the samples measured in the experiment, scaling them accurately in Excel format. **(10 points)**

a. Interpret the absorption and transmittance behavior of blue glass, including electromagnetic spectrum information. (10 points)

b. Interpret the absorption and transmittance behavior of sunglasses glass, including electromagnetic spectrum information. Find the absorption and transmittance characteristics and graphs for sunglass lenses in the literature and compare this data with your own measurement results. (25 points)

c. Interpret the absorption and transmittance behavior of window glass, including electromagnetic spectrum information. Find the absorption and transmittance characteristics and graphs for window glass used in the literature and compare this data with your own measurement results. (25 points)

* Please provide your sources at the end of your report in the references section.

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EXPERIMENT 8: PYROMETALLURGY EXPERIMENT

1. PURPOSE OF THE EXPERIMENT

- The objective of this experiment is to investigate the thermodynamic and kinetic aspects of the solid state reduction of ferrous raw materials using carbon (direct 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 iron and steel sector provides raw materials to many important industries including construction, infrastructure, automotive, white goods and machinery industries. Therefore, a strong iron and steel sector is directly associated with the level of industrialization of a country [1-3]. Iron is most abundant in the form of oxides as hematite (Fe_2O_3) and magnetite (Fe_3O_4). Removal of oxygen from the structure of oxides and transforming it to their lower oxides and/or metallic phase by using reductants (CO, H_2, C), which have higher affinity to oxygen, is called reduction. Reduction of iron oxides is conducted technologically by two different methods. The first method is the indirect reduction with CO gas resulting from the reaction of coke combustion (CO_2 formation), and reduction of CO_2 by carbon in accordance with Boudouard Reaction, in the blast furnace, which is the first stage of steel production in integrated plants and where liquid pig iron production is performed (indirect reduction). A modern blast furnace produces over 10,000 tons of liquid crude iron per day [4-6]. The other reduction method is the process in which iron oxides are converted into metallic state in the solid phase with solid or gas reductants without melting. Part of the reduction in the blast furnace occurs with solid carbon in the lower regions of the furnace. In this method, known as direct reduction, the final product is sponge iron with a high metallization rate. Sponge iron is obtained by reducing iron ore in powder, piece or pellet form below the melting temperature (at 950°C - 1100°C) using a gas or solid reducer. The total iron content of sponge iron is generally over 85% and the degree of metalization of sponge iron is between 90-95%. The carbon content of sponge iron varies between 1-2.5% and the gangue content varies between 2-4%. Apparent density of the sponge iron is ≤4 g/cm3 [9].
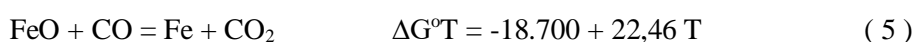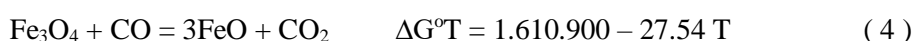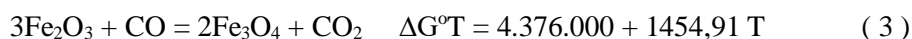
Iron ore pellets are frequently used as raw material in sponge iron production. Iron ore pellets are industrial charging materials obtained as fine-grained minerals rich in iron by agglomeration and induration. The iron pellet has higher cost than other charge elements (lump iron ore and sinter). Despite 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%) superior resistance to crumbling, uniform gas distribution and excellent reducibility of the pellets, make them one of the blast furnace's essential inputs, despite their higher cost relative to other charge elements. Furthermore, utilization of pellets in the blast furnace provides positive results including reduced coke consumption, decreased amount of slag, and increased production rate [9].

2.1 Thermodynamic Investigation of the Reduction Reaction

The carbothermic reduction of iron oxides to metallic iron, is accomplished by removal of the oxygen contained in the raw materials by deterioration of the iron-oxygen-carbon thermodynamic equilibrium to the reduction condition. In this condition, iron oxides reduce to metallic iron by the result of series reactions [4-6]. The reduction of the iron oxide in blast furnace is carried out by reductive CO gas, which is obtained by re-reacting of CO_2 gas with carbon, due to the fact that CO_2 gas, produced by combustion of carbon, is unstable at high temperatures (**see Ellingham Diagram**).

$C (k) + O_2 (g) = CO_2 (g)$ (1)

$CO_2 (g) + C (k) = 2CO (g)$ **(Boudouard Reaksiyonu)** (2)

The reduction of hematite to iron with CO/CO_2 gas mixture, takes place in three stages. The temperature-dependent empirical expressions (3), (4), and (5) of the standard free energy change (ΔG^oT) for these reactions and reactions are given below.

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

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

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

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

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

$$\Delta G_T^0 = -RTlnK_p \qquad (7)$$

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

When Fe$_3$O$_4$ and Fe$_2$O$_3$ are assumed to be pure, their activities are equal to "1". In this case;

$$\Delta G_T^0 = -RTln\frac{P_{CO_2}}{P_{CO}} = RTln\frac{P_{CO}}{P_{CO_2}} \qquad (9)$$

From this, the $\left(\frac{P_{CO}}{P_{CO_2}}\right)$ ratio which balances the reduction reactions at the T1 temperature can be calculated. The basic thermodynamic conditions for the reduction of iron oxides are $\Delta GT < 0$ and the $\left(\frac{P_{CO}}{P_{CO_2}}\right)$ ratio of the environment is greater than the equilibrium $\left(\frac{P_{CO}}{P_{CO_2}}\right)$ ratio. The Baur-Glaessner diagram and Boudouard curves drawn using reactions (2) and (9) are shown in Figure 2.1
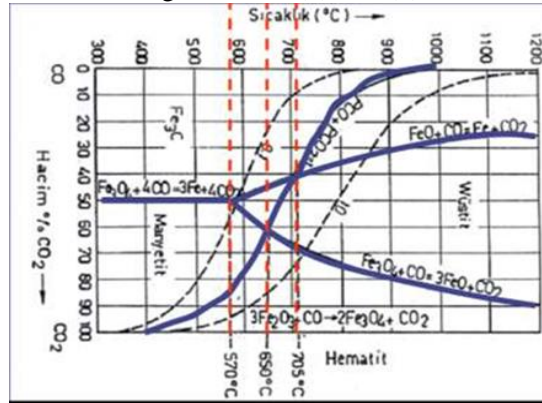

Figure 1. *Baur-Glaessner Diagram and Boudouard curves.*

According to Figure 2.1, the metallic iron reduction of iron oxides at a total pressure of P$_{CO}$ + P$_{CO2}$ = 1 atm is only possible above 705 °C. At temperatures below 705 °C Fe$_2$O$_3$ may transform to Fe3O4 and Fe$_3$O$_4$ may transform to FeO. Additionally as the total pressure of PCO + PCO$_2$ increases, the reduction temperature of the iron oxides is forced to shift to higher temperatures [4-6].

2.1 Kinetic Investigation of the Reduction Reaction

The reaction rate in a reaction can be determined by the change in the quantitative properties of a substance participating in the reaction over time. 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. Heterogeneous reactions may be gathered in five groups depending on their interface: solid-gas, solid-liquid, solid-solid, gas-liquid, liquid-liquid [9-12]. The occurrence of heterogeneous reactions between more than one phase is as follows [9,10]:

- Transport of the reducing gas to the reaction interface (diffusion)
- Interfacial reactions.
- Adsorption of the reducing gas to the reaction interface.
- Chemical reaction at the interface.
- Desorption of the products occurred after the reaction.
- 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 as "diffusion controlled", "chemical reaction controlled" and "mixed controlled" if the rate constants of these two steps are equal. 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 [9-12]. The geometric shape of the solid reacting with the liquid or gas plays an important role in determining the rate of the relevant reactions. In reactions carried out with spherical-shaped solids, the reaction interface is quite evident. As the reaction progresses, the reaction interface moves from the outer surface to the center of the part and a clear boundary is formed between the reacted and unreacted part. This model is called the reaction topochemical model or shrinking core. (Figure 2.2)
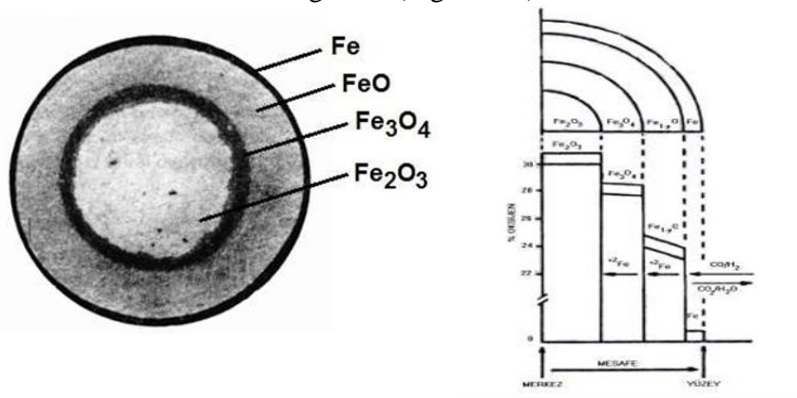

Figure 2. *Schematic representation of the reduction of the hematite particle and the topochemicality in reduction [5-7].*

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. 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 [9-12].

3. TOOL, DEVICES, and MATERIALS

Iron ore pellets and coal (coke or lignite dust), Furnace, Precise scale, Graphite crucible and charging rod, Pens and tongs.

4. EXPERIMENTAL PROCEDURES

Among the pellets produced from iron ore concentrates, identical pellets are selected and weighed. Using the total reduction reaction, the amount of carbon required for the reduction of these pellets and, accordingly, the amount of coal to be used are calculated. 150% of the theoretical amount of coal calculated on the basis of total pellet weight is weighed and used. When the tube reaches 1000°C, the pellets are buried in the coke bed prepared in the crucible and charged to the furnace with the charging rod. At the 10th, 20th and 30th minutes respectively, one pellet is taken from the furnace, cooled to room temperature and weighed with a precise scale. Reduction percentages of pellets are calculated with the formula given below.

$$Reduction\ \% = \frac{Removed\ Oxygen}{Removable\ Oxygen} * 100$$
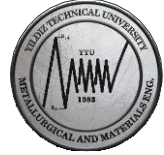
The chemical compositions of the pellets and coke used in the experiments are given below.

5. INFORMATION REQUIRED IN THE EXPERIMENT REPORT

- Write the purpose and procedure of the experiment. **(15 points)**

- Calculate the theoretical amount of coal required for the reduction of each pellet and the % reduction ratios obtained. **(20 points)**

- Draw and evaluate the % reduction rates over time graph. **(15 points)**

- Calculate the reduction rate to be achieved at the 15th and 45th minutes. **(15 points)**

- 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 observe that difference in the partially reduced iron oxide particle? Schematically draw. **(15 points)**

- Using the reactions (4) and (5), plot the % CO - temperature graphs for 700, 800, 900 and 1000 °C temperatures in the total $P_{CO} + P_{CO_2} = 1$ atm environment and name the zones. **(20 points)**

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