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<u>Editors</u> Prof. dr. coşkun özalp Assoc. prof. dr. nurettin Akçakale



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Nuclear Energy

Considering the limited fossil resources in the world and their known negative effects, the sustainability of energy resources has become an important issue. Although solar and wind energies are the first energy types that come to mind when it comes to sustainable and safe energy, it is an undeniable fact that the use of nuclear energy in electricity and heat production can be very advantageous. When nuclear energy is mentioned, situations such as nuclear accidents and radiation hazards raise concerns in people. However, as in all other energy systems, when applied properly and in a controlled manner, nuclear energy is extremely safe like other types of energy. As a result of the use of nuclear materials in nuclear reactors, medicine and industry, radioactive waste generation is of course in question. Radioactive wastes released during energy production must be managed safely, economically and in a way that people can accept. Today, with the developing technology, studies are carried out to reduce nuclear waste, and various suggestions are presented in order to reduce waste generation and to ensure that wastes are stored or destroyed in a safe manner.

The most waste occurs during the generation of energy from nuclear reactors. However, nuclear reactors still provide the most benefit. Compared to other areas of use, energy production from nuclear power plants is becoming widespread and safe in the world.

Uranium is the basic element used during nuclear power generation. However, the use of thorium and plutonium in nuclear systems is also very important. Apart from these three basic elements, zirconium, niobium, hafnium, boron carbide and cadmium, which are used as fuel clad materials, are also very important in nuclear systems.

Uranium

Uranium is the most widely used fuel material in today's nuclear reactors. Therefore, it is of great importance.

Uranium is an element that is not found in free form in nature. It combines with different elements to form uranium minerals. Although there are hundreds of uranium minerals in the earth's crust, most of them do not contain uranium economically. [1].

Uranium is the 4th element in the actinides group in the periodic table. Its atomic number is 92, it is a radioactive metal and is denoted by the symbol U. Uranium, which has a melting potential at 1132 degrees, boils at 3818 degrees. While it stands out as a hard metal with its iron appearance, it has a silver-white color.

Its name comes from the planet Uranus. It is a toxic element because it is radioactive. It is naturally mined from uranite, brannerite and carnotite mines. Worldwide, 41 thousand tons of uranium is produced annually [2].

About 99% of uranium in nature is ²³⁸U and about 1% is ²³⁵U isotopes. Of these two isotopes, only U235 can be used as fuel in nuclear power plants. Therefore, in order for the uranium ore obtained from nature to be usable in nuclear reactors, it must first be enriched in terms of U235. Apart from these two isotopes, other important isotopes of uranium are: ²³³U, ²³⁴U, ²³⁶U, ²³⁷U and ²³⁹U. ²³³U is a fissile isotope converted from ²³²Th. ²³⁶U is a neutron absorbing isotope exists in spent fuel. ²³⁹U is an element that contributes to the reduction of heat immediately after being shut down.

It is possible to divide uranium into 4 groups according to its position in nuclear reactors.

- 1. Natural uranium
- 2. Low Enriched Uranium
- 3. Highly Enriched Uranium
- 4. Depleted Uranium

These four uranium varieties are named after the differentiation of the U isotopes in their contents. While it contains approximately 0.71% ²³⁵U in its natural uranium content, it contains 99.27% of ²³⁸U and traces of ²³⁴U. Low-enriched uranium is formed by increasing the amount of uranium 235 in its natural state by enrichment methods. The ²³⁵U content of low-rich uranium can vary between 0.71% and 20%. If the ²³⁵U richness is between 3% and 5%, this fuel is also called reactor grade uranium. If the ²³⁵U enrichment is more than 20%, this uranium is called high-rich uranium. And finally, uranium with less than 0.71% ²³⁵U content is called depleted uranium [3].

Uranium can take many chemical forms. Uranium hexafluoride (UF_6) and uranium tetrafluoride (UF_4) are two of the most common. Uranium

hexafluoride (UF₆) has a very important place in nuclear technology [8]. Uranium hexafluoride is a colorless and volatile radioactive material. It is used to make fuel for nuclear power plants [9]. Although it is a solid at room temperature, it can easily change and turn into a gas or liquid. It is radioactive due to its uranium content and chemically reactive due to its high fluorine content [10]. Images of a uranium element are shown in Figure 1 [1],[3].



Figure 1. Uranium image

The use of uranium is necessary for nuclear power generation. Natural resources of uranium are widely distributed in many parts of the world. [4] Although Kazakhstan ranked first in uranium production at the beginning of the 2010s [5], Australia also has significant uranium reserves [6]. Data on uranium resources are shown in Table 1. According to the table, the approximate uranium resource in the world is 6,147,800 tons, while the cumulative production is 3,012,483 tons.

	Cumulative production (tU)		tonnes U
Kazakhstan/Uzbekistan	542,949	Australia	1,692,700
Canada	542,431	Kazakhstan	906,800
United States	374,864	Canada	564,900
Australia	232,492	Russia	486,000
Germany	217,161	Namibia	448,300
Russia	176,626	South Africa	320,900
South Africa	165,293	Brazil	276,800
Niger	152,352	Niger	276,400
Namibia	146,461	China	248,900
Czech Republic	111,214	Mongolia	143,500

France	77,015	Uzbekistan	132,300
Ukraine	69,676	Ukraine	108,700
China	55,914	Botswana	87,200
Others	148,035	Tanzania	58,200
		Jordan	52,500
		USA	47,900
Total	3,012,483	Other	295,800
		World total	6,147,800

Uranium mining is a process with many stages. As seen in Figure 2, natural uranium extracted from nature is converted to UF_6 by going through the factory, manufacturing and refining stages [6]. UF_6 is subjected to the enrichment process and enriched uranium is obtained for use in the reactor. Since it is important to convert uranium ore concentrate (yellow cake) into uranium hexafluoride UF6, there are many plants that do this.



Figure 2. Nuclear Fuel Cycle

Uranium is used not only in nuclear reactors to produce electricity, but also in the production of weapons in the war industry, in the production of hard armor and armor-piercing bullets, and in marble and ceramic factories to give color to ceramic materials.

Plutonium

Plutonium isotopes (²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu, ²⁴¹Pu) are mainly produced through sequential neutron activation reactions of ²³⁸U and ²³⁵U with neutrons of different energies [11].

Plutonium is a radioactive metallic element and its atomic number is 94. It was discovered in 1940 by scientists working to split atoms. The word "Plutonium" is derived from the planet Pluto. Plutonium is a radiological poison that can be absorbed by the body. It has five common isotopes, ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu, ²⁴¹Pu and ²⁴²Pu. All these isotopes are fissile, meaning that the nucleus of the atom can easily split if bombarded by a neutron. Uranium-239 is obtained as a result of the capture of neutrons by the natural ²³⁸U nucleus. As a result of Uranium-239's beta radiation twice, Plutonium-239 is obtained together with the Neptunium-239 isotope in the nuclear reactor.

$${}^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \xrightarrow{\beta^{-}}{239}_{92}\mathrm{U} \xrightarrow{\beta^{-}}{239}_{93}\mathrm{Np} \xrightarrow{\beta^{-}}{239}_{94}\mathrm{Pu}$$
(1)

When a reactor is used specifically to create weapons plutonium (as relatively pure plutonium-239 is preferred for the weapon), fuel rods are removed and the plutonium is separated from them after a relatively short irradiation (at low burnup). The plutonium that forms is about 93 percent ²³⁹Pu, which is referred to as "weapon grade." [12].

When uranium is irradiated in a nuclear reactor, some of the ²³⁸U captures neutrons and turns into plutonium ²³⁹Pu. It is left in the reactor for a while to allow the plutonium to accumulate. As a result, it is exposed to more neutrons. Some of the ²³⁹Pu fragments capture a neutron and transform into ²⁴⁰Pu. If the plutonium is left in the reactor long enough, this process continues: some of the ²⁴⁰Pu is converted to ²⁴¹Pu and some of the ²⁴¹Pu to ²⁴²Pu [13]. Thus, a fuel which name is "reactor grade" consisting of a mixture of plutonium isotopes is formed.

Ideal plutonium for weapons production should contain a very high percentage of ²³⁹Pu. As ²³⁸U. is bombarded with neutrons, the amount of isotopes such as ²⁴⁰Pu, ²⁴¹Pu, ²⁴²Pu increases. These unwanted isotopes make it difficult to manufacture nuclear weapons. Plutonium definitions are usually determined by the level of the ²⁴⁰Pu isotope [14].

- * Super grade; 2-3% ²⁴⁰Pu.
- * Weapons grade plutonium; 3-7%²⁴⁰Pu.
- * Fuel grade plutonium; 7-18%²⁴⁰Pu.
- * Reactor grade plutonium; over 18% ²⁴⁰Pu.

Plutonium is used to power the batteries of some pacemakers and to provide a long-lasting heat source to power space missions. Like uranium, plutonium is used for power generation in nuclear reactors. In Figure 3, there is an image of pure plutonium [15].



Figure 3. 99.96% pure plutonium ring

Thorium

Nuclear technology is basically based on the use of fissile isotopes ²³⁵U and ²³⁹Pu as fuel. The natural thorium isotope ²³²Th is converted to the fissile isotope ²³³U after a thermal neutron capture reaction. Thorium is not capable of spontaneous fission. Therefore, it cannot be used directly as nuclear fuel. The ²³²Th (thorium-232) isotope needs to be converted to ²³³U, a fissionable (fissile) isotope by swallowing a neutron.

²³²Th(fertile)
$$\xrightarrow{(n,\gamma)}$$
 ²³³Th $\xrightarrow{\beta^-}$ ²³³Pa $\xrightarrow{\beta^-}$ ²³³U(fissile) (2)

The element thorium was discovered in 1828 by chemist Jons Jakob Berzelius. Thorium was named after Thor, the Norse god of thunder. Thorium is a radioactive metal just like uranium and plutonium [6].

Although developed countries generally have uranium reserves, thorium reserves in some developing countries, especially in Brazil, Egypt and Turkey, constitute approximately 70% of the total reserves in the world. [16]. Worldwide, thorium resources are 3-4 times more than uranium resources [17]. Data on world thorium reserves are given in Table 2 [18].

Country	RAR Th (tones)	% of total
India	846.000	16
Turkey	744.000	14
Brazil	606.000	11
Australia	521.000	10
United States	434.000	8
Egypt	380.000	7
Norway	320.000	6
Venezuela	300.000	6
Other	1234.000	22
Total	5.385.000	

Table 2. World thorium reserves

Thorium can be used in warplanes engines, missiles, spacecraft, highresolution camera lenses, electronic devices, high-temperature alloys, scientific instrument lenses and many chemical processes. Thorium is a radioactive element but is also an important source of nuclear energy. Although it is accepted in scientific circles as the future nuclear fuel source, there is no commercial and economic scale nuclear facility working with thorium yet. The nature of a thorium element is shown in Figure 3 [19].



Figure 3. Thorium image

Although the most basic element for energy production in nuclear reactors is uranium, the importance of plutonium and thorium cannot be ignored. Apart from these three elements that can be used as fuel materials, there are also important elements used as control rod material and clad material in the reactor. The most widely used of these elements are zirconium, niobium, hafnium, boron and cadmium. Due to their importance in nuclear technology, it is useful to briefly introduce these elements.

Other elements

Zirkonium

Zirconium metal was discovered in 1789 by Martin Heinrich Klaproth. Zirconium got its name from the Arabic word 'zargun' meaning golden colour. Zirconium (Zr) is an off-white metal with unique physical and chemical properties. Zirconium is the 20th most abundant element in the earth's crust and is usually found in the silicate form as the mineral Zircon and less often as the oxide mineral Baddeleyite [20].

Zirconium is used in nuclear reactors to provide the outer clad for the cylindrical fuel rods that power the nuclear reaction. The main reasons for its use; low trapping cross section for thermal neutrons and good corrosion resistance. It also maintains its integrity even under intense radiation. The appearance of zirconium metal is given in Figure 4 [21].



Figure 4. Zirkonium image

> Niobium

Niobium is named after the Greek goddess of tears, Niobe, who was the daughter of king Tantalus [22]. The atomic number of the element niobium (formerly Cb), also known as "Colombium", is 41. And the element Niobium is a transition metal with a light gray color and a crystalline structure.

The main source of this element is the mineral columbite. This mineral also contains tantalum and the two elements are mined together. Columbite is also found in Canada, Brazil, Australia, Nigeria and other parts of the world.

There are studies examining the use of niobium element in nuclear technology [23], [24]. The main uses of niobium in the nuclear energy industry are; is the use of nuclear fuel, nuclear fuel alloys and structural materials of heat exchangers in nuclear reactors. Niobium alloys have both excellent mechanical strength and heat resistance and superior resistance to radiation. Niobium alloys may also be suitable for new generation nuclear fission reactors. Recent studies have shown that these materials, thanks to their superior strength properties at very high temperatures, IV. It has shown that it can be suitable in next-generation fission reactors [25]. Niobium metal is shown in Figure 5 [21].



Figure 5. Niobium image

≻ Hafnium

Hafnium is an element in group 4 of period 6 of the periodic table. The atomic number of hafnium is 72. It takes its name from the Latin word for the city of Copenhagen, Hafnia [2]. It is a shiny, silvery metal. It is located below the element zirconium, which is in the same group on the periodic table. The chemical properties of hafnium are similar to zirconium.

Hafnium, which has a very high corrosion resistance, has excellent mechanical properties. The hafnium reserves are linked to the zirconium reserves. In other words, if the zirconium reserves are depleted, the hafnium will also be depleted. Because of its high neutron absorption capacity, it is used in the production of control rods to control the fission reaction in nuclear reactors. The ability of several isotopes of the hafnium nucleus to absorb more than one neutron makes hafnium a good material for use in control rods of nuclear reactors. The neutron capture cross section of the element hafnium is about 600 times that of the element zirconium [26]. An image of hafnium metal is shown in Figure 6 [28].



Figure 6. Hafnium image

> Boron

Boron is an element with atomic number 5 and chemical symbol B. Boron is never found as a free element in nature. Boron is a non-metallic element and the only non-metal in group 13 of the periodic table elements. Although its electrical conductivity is poor at standard temperatures, it is a good conductor at high temperatures. It is a hard and black colored non-metallic solid.

Boron 10 isotope is good at absorbing neutrons. Boron is widely used as a neutron absorber material in nuclear power technology, thereby creating the possibility to control a nuclear reactor by changing the neutron multiply factor. Boron carbide is the material most commonly used as an absorbent material in control rods. This material is preferred because of its high neutron absorption efficiency, high melting point, manufacturability and relatively low cost in a wide energy range [27]. Boron image is given in Figure 7 [28].



Figure 7. Boron image

➤ Cadmium

Cadmium is a soft, bluish-white transition metal with atomic number 48 and relatively abundant in nature compared to other elements [27]. Cadmium is naturally occurring in the Earth's crust. The image of cadmium is shown in Figure 8 [29].

In the nuclear industry, cadmium is commonly used as a thermal neutron absorber due to a very high neutron absorption cross-section of ¹¹³Cd. Cadmium is used as control rod material in nuclear reactors and controls neutron flux in nuclear fission.



Figure 8. Cadmium image

Basic information about the main elements that are important in nuclear technology is shown in Table 3. The table contains information about the important isotopes of the elements, their densities, their phase state at room temperatures, their melting and boiling points and the years of discovery.

entification cards

Uranium		Plutonium	
Important isotopes	²³⁴ U, ²³⁵ U, ²³⁸ U	Important isotopes	²³⁸ Pu, ²³⁹ Pu,
			²⁴⁰ Pu
Density	19.1 g/cm ³	Density	19,816 g/cm ³
At room temperature	Solid	At room temperature	Solid
Melting point	1135 °С	Melting point	639,4 °С
Boiling point	4131 °C	Boiling point	3228 °С
Discovery	1789	Discovery	1940
Thorium		Zirconium	
Important isotopes	²³² Th	Important isotopes	⁹⁰ Zr, ⁹¹ Zr, ⁹² Zr,
			⁹⁴ Zr
Density	11.7 g/cm ³	Density	6.52 g/cm ³

At room	Solid	At room	Solid
temperature		temperature	
Melting point	1842 °C	Melting point	1854°C
Boiling point	4788 °C	Boiling point	4406°C
Discovery	1828	Discovery	1789
Niobi	um	Hafni	um
Important isotopes	⁹³ Nb	Important isotopes	¹⁷⁷ Hf, ¹⁷⁸ Hf,
			¹⁸⁰ Hf
Density	8,57 g/cm ³	Density	13,31 g/cm ³
At room temperature	Solid	At room temperature	Solid
Melting point	2477 °С	Melting point	2233 °С
Boiling point	4744 °C	Boiling point	4603 °C
Discovery	1801	Discovery	1923
Boron Cadmium		ium	
Important isotopes	¹⁰ B, ¹¹ B	Important isotopes	¹¹² Cd, ¹¹³ Cd,
			¹¹⁴ Cd
Density	2,34 g/cm ³	Density	8,65 g/cm ³
At room	Solid	At room	Solid
temperature		temperature	
Melting point	2076 °C	Melting point	321,7 °С
Boiling point	2027.00	D '1' ' /	7(7.00
Doning point	3927 °C	Boiling point	/6/ °C

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COSTS OF COLLECTION AND SEPERATION FACILITIES AND PROBLEMS FACED IN COLLECTION OF PACKAGING WASTES

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Introduction

Packaging is inevitable in our daily lives in order to save food, to reduce product damage damage and increase shelf-life and appearence. Packaging materials are also shown as one of the majör contributors for climate risk and an environmental problem in oceans and landfills (Ramchandani et al,2021).

Recovery of valuable material in waste has been targeted in two different ways (Cimpan et al.,2015):

-Separation at the source and separate collection systems

-Recovery and sorting of mixed waste at facilities taking huge amounts of wasteflow

Especially plastics packaging has gained importance in the circular economy concept. In this concept, waste materials are re-used, recycled and recovered (Eygen et al,2018).

Population growth, improvement of living standards, changing habits, social situation, development of industry, increase in people's economic income level caused an increase in waste amount (Maden,2014).

According to current economic policies in European Union has a target to increase packaging recycling rates and to reach a recycling rate of 75% for all packaging waste. It is explained that today's packaging recycling is at quite low rates, plastics reycling rates at 29% (Kleinhans et al,2021).

Especially most food packaging plastics end in waste streams after a short time of purchase. It is reported that annualy that Europe alone produces 2.3 million tonnes of plastic packaging (Ncube et al,2021).

Cimpan et al (2016) points out that sorting installations play an important role in solid waste management systems and the number of facilities increasd extensively across both Europe and North America. Altough the massive increase of these facilities, there are not enough studies on the efficiency and economic feasibility of these sorting facilites. Packaging waste brought to the sorting facilities in mixed form is divided into groups according to their types. The mixed wastes are taken to the separation band through the loading belt and subjected to mechanical or manual separation (Tozlu, 2019). Kleinhans et al (2021) indicate that collection and sorting facilities are essential because of providing high quality materials when recycling facilities are designed. Combinations of sorting units such as waste screening, ballistic seperation, magenetic seperation, air seperation, eddy current seperation, manuel sorting, sorting made with sensor and manuel sorting are used in sorting plants. They also mention that these packaging waste sorting facilities include complex processes in seperating different waste streams. It is also mentioned that

technological adavances in sorting and reprocessing steps are vital for the future recycling (Kleinhans et al., 2021). EU countries made investments in sorting and reprocessing equipment and infrastructure (Tallentire CW and Steubing B;2020).

Ayçin and Kaya (2021) emphasizes that the rates of waste recycling is still very low in Turkey and the financial support is one of the problems in waste management.

The number of studies on operational costs and faced problems of packaging waste sorting plants are quite low. Therefore the paper aims to investigate costs and significant problems of these facilities.

This Study highlights the following significant research points:

-The importance of waste pickers in waste packaging waste collection and sorting system.

-The problems of sorting facilities

-Costs of sorting facilities,

1.Packaging Waste Collection and Separation in Turkey

Packaging waste collection and separation facilities must obtain an environmental license from the ministry in order to collect packaging waste. In 2003, it first started licensing in order to ensure that the facilities that collect and recycle packaging wastes work under better conditions, to create statistical data by recording the collected and separated and recycled packaging and to modernize the facilities (Bülbül,2013). A data recording and processing system has been developed for the implementation of the packaging waste control regulation. For this purpose, a web based computer program called "Packaging and Packaging Waste" was developed by the computer experts of the Ministry of Environment and Urbanization. It has been used since 2005 (Bülbül,2013). The ways and methods to be followed in the regulation for separate collection of Packaging Wastes; It is designed to be the collection of packaging waste at its source, separate collection system for packaging waste transfer center (Eren and Erdoğan,2018).

In order to collect packaging waste, the criteria in the Packaging Waste Control Regulation issued under the Environmental Law No. 2872 must be fulfilled. Local administrations or private companies are required to obtain Environmental Permit and License Certificates as per regulation. Local governments generally transfer the collection work to private firms due to licensing conditions, collection costs and staffing difficulties. Physical conditions to be met in the Regulation on Control of Packaging Wastes are dated 27.12.2017 and numbered 30283.

Collection and sorting facilities that will operate to ensure the sorting of packaging wastes according to their types can be established in three different types. In addition to the criteria specified in the first paragraph, these facilities are required to provide the following capacities. The technical criteria and conformity assessment principles for the following types of facilities are determined separately by the Ministry.

-Facilities with a population of 400,000 or more will serve as Type 1 facilities; the total area of these facilities should be at least 3,000 m² and have a sorting capacity of at least 2000 m³/ day.

- Facilities with a population between 100,000 and 400,000 will be considered as Type 2 facilities; the total area of these facilities should be at least 2,000 m² and have a sorting capacity between 600 m³ / day-2000 m³ / day.

Facilities with a population up to 100,000 to be served are considered as type 3 facilities; the total area of these facilities should be at least 1.000 m2 and have a sorting capacity between 100 m3/day -600 m3/day.

In Type 1 collection separation facilities, at least one engineer of the environmental engineering professional group must be employed fulltime in all collection and sorting facilities. (Waste Packaging Control Regulation (AKKY, 2017). The type of facility is determined according to the population of the municipality to be served.

In accordance with the physical conditions of AAKY, published in December 2017, the location of the company to be licensed should be selected considering the distance of health protection band. Health protection band distances are provided by Provincial Health Directorates. According to the provisions of the Regulation on Opening and Working Licenses, the distance of health protection band is sought in the workplaces subject to the 1st Class Non-Sanitary Enterprise License (GSMR). Packaging Waste Collection Separation Facilities is a business place subject to 2nd Class GSMR. Since the Regulation on Opening and Working Licenses of the Workplace has the phrase "there is no permission to choose a location and establishment facility for the second and third class non-sanitary establishments", no opinion can be obtained regarding the health protection belt distances for licenses.

The date on which the deposit application will be mandatory has been determined as 1-01-2022. It was decided to establish the Environment Agency in Turkey by publishing it in the Official Gazette on 30-12-2020. In Turkey, the Environment Agency will be responsible for establishing, installing, operating or operating a deposit management system. It will carry out the activities of receiving and returning the deposit, fees and guarantees determined by the Ministry. Currently, there is no regulation

regarding the establishment of reverse vending machines in order to assist the implementation of the deposit system. It is envisaged that reverse automatons should also be included in the system and regulations should be made on the subject (Korkmaz, 2021).

2.Waste Picking

When establishing a packaging waste collection and sorting facility, it becomes important to select the machinery and equipment to be used in accordance with the packaging waste potential of the place to be installed.

There are different types of these collectors such as waste collectors, street collectors and landfill collectors. These have different socioeconomic and socio-demographic characteristics of different ages. They may be poor refugees or immigrants. In developing countries waste pickers make significant environmental and economic contributions. In addition to the collectors who turn to this job due their poverty and unemployment in the region where they live, there are also many waste pickers who collect as migrants. The number of street pickers shows an increasing trend, with the ineffective separation of resources and attractive sale prices of waste materials. The presence of unsuitable hand tools in active traffic areas creates difficulties for drivers. Foreign immigrant street pickers, which have been frequently seen recently, bring new problems. The most important of these is communucation problems. The problem caused by their lack of language is a big problem for them in understanding what they should do and should not do (www.wiego.org-occupational groupswaste pickers). Velis (2017) and Wilson et al. (2006) mention that waste management and recycling activities are informal in the low-income and middle-income countries of Africa, Asia, Latin America and Caribbean Boini-Rocha et al. (2021) also mentions that the population of recyclable material waste pickers living in low-income countries is fifteen million. Waste pickers or scavengers extract recyclables from mixed wastes. They are labor-intensive force for recyclables (Gall et al,2020). The Ministy of Labor includes the recyclable waste picker in the Brazilian Occupation Code since 2002.

Keser (2010) reveals that relationships with acquaintances and relatives in today's urban areas now provide the possibility of surviving for those migrating to urban. Urban areas have changed along with the altering economical and social policies. The most disadvantaged group influenced by these economical and political changes in urban areas is the new poor groups of urban who are looking for a work in order to survive and are far from all of the secure works in urban areas. Street waste pickers, in this context, is one of the new poor groups of urban and they do this business in order to survive.

3.Methodology and Data Collection

A survey was used a research method for collecting data from 27 collection and seperation facilities to gain information and insights into various problems of interest. The survey was conducted in Çorlu Town, a developing town with an increase in waste and packaging waste because of population growth resulting from rapid industrialization after 1990s, with a population of 280000 in Turkey. The process involved a questionnaire with open-ended questions which were made face-to-face. Information generated packaging waste collection and seperation survey will be useful to administrators/policy makers in order to have an efficient collection and sorting system. Detailed operation costs were examined in one of the sorting plants. The resarch included a search for getting information about waste pickers. The data collection technique included an interview and observations with waste pickers.

4. Results and Discussion

4.1.Education and Awareness

Within the scope of the packaging waste management plan, training and awareness raising activities are carried out periodically about the collection equipment that is distributed / placed in certain places and about the collection of packaging waste at the source, periods of collection. Faceto-face studies are done by touring from door to door in certain periods. Awareness raising is also included in television channels as a public spot.

Education and awareness raising activities are generally carried out for primary and secondary education. However, since the trainings are not done frequently, it does not help much. Trainings held once a year are forgotten in a short time. Citizens who perceive and appeal as municipalities' earning gates are encountered in the collection works carried out during the information activities done by door to door. Citizens who expect services such as infrastructure, roads, water, electricity from municipalities do not help considering that these services should be a priority and not domestic wastes a priority. Education and awareness should not be dealt with domestic wastes.

4.2.Waste Pickers

Waste pickers are the ones who earn their living by collecting recyclable wastes such as paper, plastic, glass, metal from the streets, garbage and selling them to the recycling facilities. Street pickers do not have anything like health guarantees or social rights. They usually collect waste by wandering the streets early in the morning and in the evening after work, when waste is thrown into the garbage. In the street collection system in Turkey, despite the existence of registered firms, unlicensed collectors (unlicensed /waste pickers) demonstrate activities. They work on average 7-8 hours a day. They earn around 15\$-25 \$ in a day. Street collectors are generally made up of people who come from their villages to work in metropolitan areas, but cannot find jobs as they wish and cannot return to their villages. Recently, they are street pickers from foreign citizens coming from countries such as Syria, Afghanistan and Georgia. Street collectors wander streets and collect waste with a 1000 m³ volume sack attached to a metal skeleton and change the average of 4 sacks per month. Street collectors take the wastes that can be evaluated by mixing the waste that is thrown away in the residences and markets. Pickers, who could not have another opportunity to work, go to the streets among people and collect waste again with the collection equipment called as rickshaw that they easily find.

Although the Ministry of Environment and Urbanization prohibits the purchase of packaging wastes from street collectors in 2016, collecting and separation facilities continue to receive waste from street collectors, even if they are unregistered, due to a financial income obtained.

4.3.Collection and Sorting Costs of Collection and Seperation Facility

Within the scope of this study, the establishment and operating costs of a collection separation facility operating in Tekirdağ province were investigated. According to 2018 data of a collection separation plant operating in Tekirdağ province, the costs of collecting and sorting waste are as follows;

- Facility investment cost
- Land and construction costs
- Segregation band
- Press machine
- Lightning Rod
- Weigher
- At least 2 trucks, forklifts or buckets, passenger vehicles
- Office supplies (furniture, computer, printer, camera system)
- Collection equipment (indoor box, container, cage, bag)
- Personnel cost (salary, insurance, meals, work clothes, travel)
- Vehicle cost (fuel, maintenance, insurance, tracking systems)
- Facility internal cost (electricity, water, natural gas, consumables)

In return for the expenses incurred due to the collection and separation of wastes, there is an income arising from their sale as raw material after separation. In order to provide income and benefits economically, the amount of sales must be greater than the expenditure.

4.4.Vehicle Costs

The vehicles used for the collection of packaging waste and their average costs for a collection and separation facility are given in Table 1.

İtem No	Cost Types	\$/month	\$/year
1	Fuel Expenses	4815	57780
2	Maintenance Expenses	1815	21780
3	Insurance Costs	1400	16800
4	Vehicle tracking system	88	1056
	Total	8118	98472

Table 1. Vehicle Costs

The routes of the collecting vehicles are important in terms of fuel economy. If they do not operate on certain routes and in certain patterns, especially increases in fuel amounts occur. Vehicle tracking systems are important in terms of monitoring this process.

4.5.Personnel Cost

Minimum personnel and job descriptions to be employed for the collection of packaging wastes are as in Table 2. According to Table 2, a total of 17 personnel work at the collection and sorting facility. It is seen that 12 of these personnel are involved in the separate collection of packaging wastes at the source and the separation of them according to their types at the facility.

Personnel	Number	Job Description
Driver	2	Using vehicles in the collection of packaging waste
Collection personnel	4	Working behind the truck in the collection of packaging waste, loading the waste
Separation Personnel	6	Separating the packaging wastes brought to the facility according to their types on the separation band
Forklift/Bucket Operator	1	Carrying out the loading, unloading operations of the wastes in the facility
Accounting Personnel	1	To follow the accounting transactions of the facility
Environmental Engineer		In line with the packaging waste management plan, to follow the management of packaging waste in the field, to keep the waste data recorded, to participate in the inspections with the Municipality personnel, to place the waste collection equipment at the relevant points, to follow up the negativities in the field and notify the necessary places, to ensure and monitor the current operation of the facility.

 Table 2: Personnel working at Facility

Personnel	Number	\$/month	Total \$/year
Driver	2	1120	13440
Collection Personnel	4	1640	19680
Separation Personnel	6	2460	3120
Forklift/Bucket Personnel	1	560	6720
Safety Personnel	1	460	5520
Accounting Personnel	1	490	5880
Environmental Engineer	1	715	8580
Total		7445	89340

Salaries paid to the personnel working within the licensed company are shown in Table 3.

 Table 3: Personnel Costs

4.6.Expenses

Expenses such as electricity, water, telephone, food, stationery etc. during the operation of the facility are given in Table 4.

Number	On-Site Cost	\$/month	\$/year
1	Electric	410	4920
2	Water	80	860
3	Telephone	155	1860
4	Stationery	410	4920
5	Food	585	7020
6	Rent	2040	24480
Total		3680	44160

 Table 4: On-Site Expenses

4.7. Problems Encountered During Licensing Procedures

One of the common problems in licensing is the lack of a suitable place. The areas of 1.000 m^2 , 2.000 m^2 and 3.000 m^2 needed as a surface area are generally difficult to find. Infrastructure and road problems are among the frequently encountered problems. Inter-institutional communication problems also cause problems in terms of bureaucracy. Failure of the institution to approve or agree with the opinion / text given by one institution makes the progress difficult.

A weighbridge program that provides remote access with internet connection was another problematic situation required by Packaging Waste Control Regulation. After the regulation came out, it was difficult for the software companies to make appropriate software, and the license applications had problems. It was not clear what kind of a program it would be, whether the computer was connected to the scale or a connection to the program. It was understood that after a period of about 6 months, the program to be installed on the computer to which the scale is connected will be connected remotely with a user name and password. During this time, companies have had difficulties to obtain licenses. Another problem is the phrase "The facility will be surrounded by permanent building material". The absence of information such as what is desired as a permanent building material and how high it should be surrounded created an uncertainty process.

The facility must have a separation band to separate mixed packaging waste. The separation band should be designed to meet the capacity and specified in the capacity report. In the capacity report, there is information to determine the capacity such as the length, width of the separation band and the feed rate of the band. However, although the declaration systems such as collection, recovery, waste declaration, waste amounts of packaging waste of the Ministry of Environment and Urbanization are all by kilograms, it is requested to calculate the capacity of the separation band in cubic meters. However, although the cubic meter data is not used in any system, why the account is requested is still unknown.

4.8.Survey Results

Collection and separation of packaging waste is a laborious and long process. In this process, a survey was conducted with 27 companies working in the industry in order to better understand the problems and problems faced by licensed companies. In line with the survey, 84% of the companies operate in this sector over 10 years, 8% between 5-10 years, 8% less than 5 years. They have been generally engaged in this business for more than 10 years. Those who work under 10 years also continue as a father's profession.

In other words, waste work usually appears as a sector passed from father to son. With Packaging coming into force in 2011, most companies started their license processes and got their 5-year licenses. A licensee company renews when the license expires.

According to the results of the survey, 10% companies in the sector work in the sector for only 0-5 years, and 85% of them say that this is due to the low level of local government support. 92% of companies say that waste collection costs are high. 70% of the licensed companies stated that the licensing period is normal (average 6 months). Administrative fines were imposed on 92% of the firms working in the sector within the framework of environmental law. 97% of licensed companies say that separate collection at the source is inefficient. 100% of the companies receive waste from street waste pickers and at least accept the waste coming to their facilities economically. 100% of companies stated that they suffered from infrastructure. In general, they complain that there is no sewer system that can discharge domestic waste water originating from the personnel, and that there are few treatment facilities to be sent after the waste water accumulated in the septic tank pits is removed. The companies make agreements with the municipalities after getting the license. When companies that prepare Packaging Waste Management Plan together with the municipalities quickly encounter difficulties in the field, they gradually move away from the municipal works and head towards the industry. Factors such as investment costs, personnel and operating expenses, street collectors drive licensed companies away from municipal works.

Most companies in the industry are not satisfied with waste collection costs. Companies, wishing to collect in collection equipment such as indoor boxes, cages built on the field for the return of packaging waste, complain that waste pickers collect from these equipment and sell again to companies and also disposal of household waste to these equipment.

In addition, the payment of fuel, personnel, and business costs in advance poses a serious burden. A lot of investment is required from licensed companies that want to be included in the Packaging Waste Management Plan. Apart from indoor boxes, containers, cages, new trucks, external demands such as aid, donation, sponsorship to the municipality are also burdens. However, preparing a management plan and collecting is primarily among the duties of the municipality. In addition, municipalities are required to show licensed companies suitable places for their work.

Most firms have been punished more or less under the Environmental Law. Some have been fined in various amounts due to their unlicensed work, some due to lack of information documents. Although the work done is a dirty and difficult job, besides these difficulties, fining of penalties makes the companies unofficial.

Separate collection work in the source is said to be inefficient. The reasons for this are not being collected separately from domestic wastes in residences, markets, institutions / organizations, where packaging wastes occur, either by disposing of them with domestic wastes or by throwing them into packaging waste containers together with domestic wastes. Also, waste collection of street waste pickers causes inefficiency for licensed companies. Although they are against street waste pickers, street waste pickers collect a considerable amount of waste. Firms that have invested in this business have to buy the wastes that street collectors bring to their facilities by paying in one way or another.

The facilities are generally set up for those who are far from residential areas. This situation brings along road and infrastructure problems. The use of soil and rough roads causes both dust and malfunctions in vehicles. Being away from the settlement place, the sewage systems for domestic wastewater have not yet been formed and the use of septic tanks is required. The issue of discharging filled septic tanks is also a problem.

5.Conclusions and Recommendations

The fact that packaging waste is a large sector means that the amount of waste is very high. Too much waste means a lot of consumption and too much consumption means a rapid depletion of natural resources. Most of the packages produced today are produced by consuming natural resources. In order to prevent the consumption of natural resources and reduce environmental pollution, packaging wastes must be managed correctly and they must participate in the recycling cycle as necessary

One of the reasons why companies working in the sector for many years have problems in the licensing stages is that the institutions and organizations that issue regulations act independently and unaware of each other. In addition, regulations issued without fully determining / knowing the operation in the field create difficult situations to be followed. In the same way, the processes are getting longer because the inspection mechanisms cannot evaluate the situation in the field and they directly adhere to the regulations. This increases informal work.

Provincial Directorates of Environment and Urbanization, which constantly inspect a licensed company, do not inspect unlicensed firms unless there are complaints. This situation makes people choose to work informally.

Local governments consider collection and separation facilities as dumps. For this reason, problems arise during the licensing stages. Collection and separation plants, whose working areas are not shown, try to establish facilities with their own means. This is a financial burden. When there is not enough investment in the facility, the outside images are bad. If local governments allocate a place for such facilities in their development plans, collection and separation facilities will also be able to work in a clean and orderly manner.

With the support of local governments, road and infrastructure problems will be eliminated. In this way, licensing processes of collection separation facilities will be more efficient and faster.

Street waste pickers continue to be a bleeding wound, both socially and economically. There are many people who work in unsanitary conditions, without social security, without even a place to sleep. Municipal police officers try to prevent these people but they cannot cope because they are numerous. In fact, street waste pickers collect significant amounts of waste and put them in a recycling cycle.

If projects are carried out to include these people in the system, both unregistered waste collection will be eliminated, and the lives of people who will do this work more like a job will be regulated. The Ministry of Environment and Urbanization continues to work on removing street collectors from the system. In this way, informality accelerates. It should not be forgotten that street collectors are an important part of the collection system and should somehow be included in this system. Various ways such as card system, premium over kilogram should be tried.

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Chapter 3

6

THE USAGE OF HEAVY METALS IN COLORATION OF (DYEING) TEXTILE MATERIALS AND INVESTIGATION OF THEIR EFFECTS ON HUMAN HEALTH

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1.INTRODUCTION

The textile industry is one of the leading industries in the world in terms of pollution. A large amount of chemicals are used in this sector. For example, in the production of color pigments of textile dyestuffs heavy metals such as lead, chromium,cadmium and copper are widely used.

About two thousand different chemicals are used in the production of dyestuffs in textile industry.

Catalysts are used in the synthesis of dyestuffs and the residues of antimony(Sb), copper(Cu) and chromium(Cr) remain in dyestuffs. Some reactive dyestuffs contain metal compounds such as copper(Cu), nickel(Ni), cobalt(Co) and chromium(Cr). Metal-free dyestuffs contain metallic impurities resulting from raw materials during their production.

Metals are used in the manufacture of some dyestuffs and pigments. Metals can be transmitted to

textile materials by dyeing and finishing processes. Different types of dyestuffs are used in the coloration of textile products.

The main heavy metals used in the coloration of textile materials are classified as arsenic(As),cadmiyum(Cd), cobalt(Co),chromium(Cr), copper(Cu), nickel(Ni), lead(Pb), selenium(Se), titanium(Ti) and zinc(Zn).

1.1. Chemical Structures and Properties of Heavy Metals

Dyestuffs are used in the coloration of textile products. However the dyestuffs used in textiles are organic.Inorganic natural dyestuffs such as $Fe_2O_3, Cr_2O_3, Pb_3O_4, HgS$, graphite etc can be given as examples. Generally dyestuffs give chemical or physicochemical reaction with the surface of the textile materials.

Heavy metals such as arsenic(As), lead(Pb), cadmium(Cd), cobalt(Co), nickel(Ni), copper(Cu), mercury (Hg) are found in the dyestuffs used in coloration. In addition they can pass into the fiber as a result of absorption from the soil and air. These substances must be used below a certain level (ppm) so that they not show toxic properties.

Mordant dyestuffs are used to improve the substantivity of natural dyestuffs to fibers. Mordants bind the dyestuff to the fiber. Metals such as Fe, Co, Cu, Cr which are the transition atoms in the periodic table, form a complex with dyestuff molecules. This results in matte color shades. In the complex compound the metal atom both bonds with the fiber and interacts with the fiber as a result of orientation. As a mordant in coloration in the textile industry salts such as aluminium(Al), tin(Sn), iron(Fe) and chromium(Cr) which form water-insoluble hydroxides are used. Primarily, the salts of elements such as aluminium(Al), chromium(Cr), iron(Fe),

copper(Cu), tin(Sn); mordant substances such as tartaric acid, ammonia and tannin are absorbed into the fiber. The dyestuff is applied to the fiber and the dyestuff is attached to the fiber with the mordant. Many natural and synthetic dyestuffs are in this class. Synthetic ones are usually derived from anthracene. They do not have direct affinity for textile materials .The chemical structure of the mordant dye that forms a complex with the Al cation is given in Figure 2. It creates red with A1⁺³, dark purple with Fe⁺², brown-black with Fe⁺³,red-purple with Sn⁺², purple with Sn⁺⁴ and brownpurple with Cr⁺³. High fastness red tones are used as Al-Ca mordant with alizarin on cotton. Mordant dvestuffs contain acidic and basic functional groups. They form unstable compounds with vegetable and animal fibers. In order to ensure better fixation of the dyestuff, pretreatment is performed with Al, Sn, Fe and Cr salts(mordant) before dyeing. After adding chromium compounds, dyeing is carried out. These dyestuffs contain binding groups to form methyl complexes with aluminium(Al), chromium(Cr), cobalt(Co), copper(Cu), nickel (Ni) or iron(Fe)salts (EPA,1996). The most important mordant dyestuffs are natural dyestuffs .Their main coloring matter is alizarin . Alizarin Red (AR) an anthraquinone dyestuff is an anthracene derivative that dissolves well in water) (Liu ve ark., 2015). It is widely used in textile industry. The structure of Alizarin Red is given in Figure 1.



Figure 1. The structure of Alizarin Red (AR)(Liu vd., 2015)

The chemical structure of the Al-complex mordant dyestuff is shown in Figure 2.



Figure 2. The chemical structure of the Al-complex mordant dyestuff (Başer vd., 1989)

Heavy metals in the textile industry are also found in the structure of metal complex dyestuffs. A metal atom(Cr, Cu, Co or Ni) forms strong complexes with one or two dvestuff molecules. Metal complex dvestuffs contain an azo group in their structure. (Brown, 1987). Co, Cr, Cu and Ni ions are used as metals in metal complex dyestuffs . These dyestuffs are divided into two groups as 1:1 and 1:2 metal complexes. 1:1 metal complex dyestuffs contain one or two -SO₂H groups and they are applied to the fibre in a strongly acidic condition. 1:2 metal complex dyestuffs contain polar groups such as -SO₂CH₃ or -SO₂NH₂ to ensure sufficient solubility of the dyestuff in water (Baser, 1990; Özcan, 1978). Uncomplexed dyestuffs have a planar structure. They are mostly used for dyeing protein and polyamide fibers . In these dyestuffs azo group with metals form a complex such as chromium-mordant, metal chromium and final chromizing method. The biggest disadvantage is that the process is done in two stages. Dyestuffs that form complexes with chromium, cobalt, rarely copper or iron cations form metal complex structure by heating with metal salt solutions at 70 °C and at appropriate pH.) 1:1 metal complex dyestuffs contain 1 metal atom and 1 dyestuff molecule (CI Acid Blue158); in 1:2 metal complex dyestuffs 1 metal atom contain 2 dyestuff molecules (CI Asit Violet 90, CI Asit Black 60). The chemical structure of metal complex acid dvestuffs are given in Figure 3.



C.I. Acid Violet 90

Figure 3. The structure of metal complex acid dyestuffs (Tutak, 2007)

The complex formation structures of the Cr atom are shown in Figure 4.



Figure 4. The complex formation structures of the Cr atom (Tutak, 2007)

And also the structure of the alizarin-chromium complex dyestuff is given in Figure 5.



Figure 5. The structure of the alizarin-chromium complex dyestuff (Özcan, 1984)

As an example of metal complex dyestuffs, direct blue 93 dyestuff which forms a complex structure with copper atom is given. The chemical structure of the direct blue 93 dyestuff is given in Figure 6.



Figure 6. The chemical structure of the direct blue 93 dyestuff (Tutak, 2007)

In the textile industry, heavy metals are found in the structure of chromium complex dyestuffs that are insoluble or slightly soluble in water. At the end of this process called chroming; light and wet fastnesses of monoazo dyestuffs increase. With this process, a negative change in the color of the dyestuff is observed. Acid mordant dyestuffs are used for dyeing wool and polyamide fibers. First, the acid dyestuff is attracted onto the fibers. After that, the dyeing is completed by chroming . With this process, the hydrophilic groups in the dyestuff molecule form complex compounds with the chromium cation. The Cr(III) and Co(III) ions with coordination number of 6 in the chroming process, it forms 1:1 and 1:2 complex compounds. Chromate or dichromate salts in chromium azo dyestuffs react with the sistine bonds in the structure of the wool. The chemical structure of the azo acid chromium salt dyestuff is shown in Figure 7. The concentration of hydrogen ions in the structure affects the complex structure.



Figure 7. The structure of the azo acid chromium salt dyestuff) (Başer vd., 1989)

The chemical structure of 1:1 chromium complex dyestuff is given in Figure 8. 1:1 metal complex dyestuffs have one or two sulfonic groups for water solubility.



Figure 8. The chemical structure of 1:1 chromium complex dyestuff (Başer vd., 1989)

Since the bond formed in the alizarin-chromium complexation is a covalent bond, the compound is not ionized. The trivalent chromium ion combines with three molecules of alizarin. The other bond given in the second step and indicated by the arrow is the coordinate covalent bond. With the coordinate covalent bond, a 6-membered ring is formed and the stability of the compound increases.

In the metal complex dyestuff molecule, the structure loses proton and consists of the neutralization stage. Chromium complex dyestuffs have higher dyestuff stability than copper complexes. The chemical structure of 1:2 chromium complex azo dyestuffs are given in Figure 9a and 9b.



Figure 9a. The structure of asymmetric 1:2 chromium complex azo dyestuff) (Walter, 1983)



Figure 9b. The chemical structure of 1:2 chromium complex azo dyestuff (Law vd., 1993)

In the o,o' parts adjacent to the azo group in the structure, the dihydroxy, hydroxy-methoxy, carboxy-hydroxy groups react with $CuSO_4$ in a weak acidic condition, to form copper complexes. The chemical structure of the azo acid copper salt dyestuff is shown in Figure 10.



Figure 10. The structure of the azo acid copper salt dyestuff (Başer vd., 1989)

o,o'-dihydroxyazo dyestuffs form metal complex dyestuffs at suitable conditions with metals such as chromium(Cr), cobalt(Co),nickel(Ni) and aluminium(Al). The chemical structure of o,o'-dihydroxyazo dyestuff is given in Figure 11.



M=Co, Ni, Cu, Zn

Figure 11. The chemical structure of 0,0'-dihydroxyazo dyestuff (Erdem vd., 2007).

A double hydroxyl, a carboxyl or a hydroxyl and an amino group must be present at the o,o' positions of the azo group in the complex azo dyestuff molecule. Some dyestuffs contain an azomethine group instead of an azo group. The atom participating in the complexing is the nitrogen atom. The structure of the o,o'-chromium complex dyestuff is shown in Figure 12.



Figure 12. The structure of the 0,0'-chromium complex dyestuff (Beffa, 1984)

Azo dyestuffs with complex structure such as o,o'-dihydroxy, o-hydroxy-o'-amino and o-hydroxy-o'-carboxy, Fe(II) and Fe(III) salts or complexes form 1:2 metal complex dyestuffs under suitable conditions. The structure of the o,o'-dihydroxyazo-Fe(II) metal complex dyestuff is given in Figure 13.



Figure 13. Structure of 0,0'-dihydroxyazo-Fe(II) metal complex dyestuff (Özkınalı, 2002)

In outer complexes, azo groups do not participate in complex formation. 1:1, 1:2 and 1:3 structures can be obtained depending on the metal ion and oxidation step of azo compounds containing mostly salicylic acid. Since the azo group does not participate in the complexing in salicylic acid derivatives, there is no significant increase in light fastness and no specific change in color tone is obtained as a result of combination with metal ions. The chemical structures of outer complex dyestuffs are shown in Figure 14.



Figure 14. The chemical structure of outer complex azo dyestuffs (Kabay, 2002)

If one of the nitrogen atoms in the azo group acts as an electron donor, the color of the azo compounds changes significantly during complex formation(Finar,1973). Due to its strong electropositive property, the metal ion changes the electron distribution in the dyestuff and the absorption spectrum of the molecule also changes.

Heavy metals used in coloration in textile industry are also found in the structure of solvent dyestuffs that do not dissolve in water. These dyestuffs are soluble in low polarity solvents and polar solvents such as alcohol. They have different chemical structures such as azo, azo metal-complex, triaryl-methane and anthraquinone. The structure of azo compounds are simple. They are usually yellow, orange and red in color. The chemical structure of the solvent dyestuff soluble in solvents such as alcohol, ester, glycol and ketone is given in Figure 15.



Figure 15. The chemical structure of the solvent dyestuff (Finar, 1973)

Heavy metal salts are also found in the structure of nitroso dyestuffs. Nitroso compounds have a tautomer structure. Tautomer is a special structural isomer that can convert to each other. The tautomer structure of the nitroso compound is shown in Figure 16.



Figure 16. The tautomer structure of nitroso compound (Wang vd., 1991)

Nitroso compounds are divided into two groups such as ortho-nitroso and hydroxy nitroso. The ortho-nitroso dyestuff molecule forms a complex compound with the metal ion. The chemical structure of ortho-nitroso metal complex dyestuff is given in Figure 17.



Figure 17. The chemical structure of ortho-nitroso metal complex dyestuff (Başer vd., 1989)

Heavy metal salts form complex compounds with hydroxy-nitroso dyestuff molecules. If these compounds contain sulfone groups, they have acid dyestuff character. The structure of hydroxy nitroso-iron complex dyestuff is shown in Figure 18.



Figure 18. The structure of hydroxy nitroso-iron complex dyestuff (Başer vd., 1989)

Heavy metals in the coloration of textile materials are also used in the production of triphenylmethane dyestuff. The light fastness of triphenylmethane dyestuffs is high. The chemical structure of triphenylmethane dyestuff is given in Figure 19.



Figure 19. The chemical structure of triphenylmethane dyestuff (Özcan and Ulusoy, 1978; Gohl and Vilensky, 1984)

Heavy metal is also present in the structure of the azomethine dyestuff. These dyestuffs are divided into three groups as neutral, cationic and anionic azomethine dyestuffs. The chemical structure of anionic azomethine dyestuff is shown in Figure 20.



Figure 20. The structure of anionic azomethine dyestuff (Hinks vd., 2001)

It is also used as Cu-phthalocyanine dyestuff. Phthalocyanine derivatives have a wide color shades. Almost 90% of phthalocyanines are used as pigment dyestuffs. Phthalocyanine dyestuffs are also used as ingrain dyestuff in textiles. As a result of the reaction phthalocyanine with copper(Cu) or nickel(Ni) salts, metal complex pigment dyestuff is obtained. Cu-phthalocyanine and its halogenated derivatives constitute 25% of all organic pigments. It is in bright blue shades. They are resistant to acid, base, reducing, oxidizing and organic solvents. Cu-phthalocyanine sublimes without decomposition at 580 °C. The colors of metal phthalocyanines are usually blue-green. Phthalocyanine chromophores have strong encolouring properties. Phthalocyanines that do not form metal complexes absorb between 664-699 nm. Maximum absorption point at metal phthalocyanines depends on the metal atom. The most used metal atoms are copper, iron, cobalt, nickel and zinc. The structure of Cu-phthalocyanine dyestuffs are given in Figure 21.



Figure 21. The structure of Cu-phthalocyanine dyestuffs (McKeown, 1998)

The copper(Cu) metal phthalocyanines are red-tones; nickel(Ni), cobalt(Co), zinc(Zn), aluminium (Al), beryllium(Be), tin(Sn) and lead(Pb) complexes have green-shades. The chemical structure of Ni-phthalocyanine dyestuff is shown in Figure 22.



Figure 22. The chemical structure of Ni-phthalocyanine dyestuff (Sugimori vd., 1998)

With the addition of a sulfo group to Cu-phthalocyanines, a class of dyestuffs called phthalocyanines are formed. These dyestuffs are used as sodium salts of disulfonic acid(direct dyestuff).Trisulfone derivative of copper(Cu) phthalocyanine (Coomasssie Turquoise Blue 3G) can be given as an example of this group. Light fastness is higher than that of triphenylmethane acid dyestuff. The chemical structure of copper(Cu) phthalocyanine trisulfone dyestuff is given in Figure 23.



Figure 23. The chemical structure of copper(Cu)phthalocyanine trisulfone dyestuff (Özcan, 1978)

Some phthalocyanines are used as a vat dyestuff. For example, the reduction product of Co-phthalocyanine has high affinity for cellulosic fiber in basic solution. They have a reduction-oxidation reaction. Its light and washing fastness is high. The reduction-oxidation reaction of the Co-phthalocyanine dyestuff is shown in Figure 24.



Figure 24. The reduction-oxidation reaction of the Co-phthalocyanine dyestuff (*Başer vd.*, 1989)

Some heavy metals in the textile industry are also found in the structure of metal-complex carbonyl dyestuffs. These dyestuffs are also called mordant dyestuffs. The metal cations required to form the complex are Ni(nickel),Co(cobalt) and Cr(chromium). These metal cations are applied to the fiber either during dyeing or after dyeing. The most important dyestuffs of this class are natural dyestuffs. Alizarin group gives color to these dyestuffs. It is used with different mordants. They are produces dark purple, brown-black, red-purple, purple and brown-purple shades among them were Fe⁺², Fe⁺³, Sn⁺², Sn⁺⁴ and Cr⁺³ respectively. The chemical structure of Ni(nickel)-carbonyl dyestuff is given in Figure 25.



Figure 25. The chemical structure of Ni(nickel)-carbonyl dyestuff (Tutak, 2007)

1.2. The Usage of Heavy Metals in Coloration of Textile Materials

Incolorationoftextilematerials mordants such as Al(aluminium), Sn(tin), Fe(iron) and Cr(chrome) salt hydroxides of water insoluble are used. Today, chromium salts are used for dyeing wool fiber. They are used for dyeing wool, leather, silk and paper. Many mordant dyestuffs contain azo, oxazine or triarylmethane compounds (Karaca, 2006). Oxazine dyestuffs give metal complex compounds with chromium. It is used as a mordant dyestuff in printing and dyeing of wool (EPA, 1996).

Metal complex dyestuffs in coloration of textile products are used in dyeing and printing of wool, polyamide, cellulosic fibers, silk, leather and polypropylene fibers with metal complex dyestuffs. It is divided into two groups such as 1:1 and 1:2 metal complex dyestuffs. They have high light and washing fastness. With the formation of metal complexes, the solubility groups in the dyestuff molecule are blocked. Washing and light fastnesses increase, perspiration fastness decreases. As a result a matte appearance is obtained in the color shade of dyestuffs. Heavy metal cations that may remain on the fiber form peroxides affected by the washing agents and the air oxygen in the basic condition. Their usage damages the fiber structure. Colors of metal complex dyestuffs are matte. Chromium, cobalt and copper complexes are used in textile dyestuffs. Iron complexes are used as a leather dyestuff. Nickel complexes are used in pigments.

Metal complex carbonyl dyestuffs are used as a pigment dyestuff in the dyeing of polypropylene. 1:2 chromium complex azo dyestuff is a black and dark blue dyestuff used in the dyeing of polyamide and wool. (Walter, 1983). It has high light and washing fastness.

Metal complexes of o,o'-dihydroxyazo dyestuffs with chromium and cobalt are used in electrophotography. These dyestuffs have good washing and light fastness properties on protein and polyamide fibers (Hsieh,1990; Wang,1991). Metal complexes of these dyestuffs are used in dyeing and printing of polyamide fiber.

Complex compounds formed by hydroxynitroso dyestuffs with heavy metal salts have pigment or acid dyestuff character. Light fastness of the 1-nitroso-2-naphtol with Fe⁺² complex (Pigment B) is good. The sodium salt of 1-nitrozo-2-naphtol-6-sulfonic acid with iron complex is Naftolgrun B. It is used for dyeing wool and silk fiber. In addition, this dyestuff's color is dull and is used as a military camouflage material.

Cu-phthalocyanine dyestuffs are used for pigment dyestuff, printing inks, emulsion dyestuffs and dyeing of leather. It is also applied to textile printing. Polychlorinated copper phthalocyanine derivatives are also used for coloring polymers such as acetate, polyethylene and polypropylene.

Some phthalocyanines (vat dyestuff) are used in dyeing and printing of cellulosic fiber.

Chromium complex dyestuffs are used in wool, polyamide; copper complexes are used in cotton and leather dyeing (Vardar, 2006).

Solvent dyestuffs are non-ionic dyestuffs and they are used to dye soluble materials such as plastics. Most solvent dyestuffs are di azo compounds (Karaca,2006).

1.3. The Usage of Heavy Metals In The Coloration of Textile Materials and Some Related Studies

There are many studies on the use of heavy metals in the coloration of textile materials. The articles obtained from the literature review are summarized:

Szurdoki et al.(2000) have examined that the selectivity of chelating azo dyestuffs to seven heavy metals (Cd⁺², Cu ⁺², Fe⁺²,Hg⁺²,Ni⁺²,Pb⁺²and Zn⁺²) using UV-vis spectroscopy. Szurdoki et al. determined that the synthesized azo dyestuff compound was more selective in Hg⁺² ion.

Rezvani et al.(2006) in their study investigated the liquid crystal properties of azo copper complex dyestuff containing salicyldiamine functional group by DSC analysis. In the DSC analysis of the copper complexes obtained for endothermic transitions have been detected. The first of these show the transition from one crystal structure to another. The third value indicates the transition from the crystalline phase to the mesophase, the fourth transition from the mesotropic phase to the isotropic liquid. As a result of the investigations, they found that all copper complexes were in liquid crystal structure.

Seu et al.(1984) in their study investigated cotton dyeing properties and fastness properties of some heterocyclic azo disperse dyestuffs containing thiazole ring.

Freeman et al.(1990) in their study, investigated the degradation properties of chromium complexes of 0,0'-dihydroxy azo dyestuffs.

Kocaokutgen et al.(1998) in their study synthesized metal complexes of o,o'-dihydroxy azo dyestuffs and dyed wool fiber.

Gumrukcuoglu et al.(1990) in their study; applied the basic β -naphtol solution to the cotton fabric. Azo dyestuffs were applied to cotton textile material by reacting with diazonium salt solutions of aniline, toulidine, naphthylamine and amino azo benzene. By obtaining reactive dyestuffs from various heterocyclic compounds, they produced dyestuffs with high fastness properties.

Mahapatra et al.(1997) in their study; Zn, Cd and Hg metal ions formed complex compounds in tetrahedral geometry. The obtained complex compounds were used to dye wool fiber. Good washing and light fastnesses were obtained after dyeing.

Erdem et al.(2007) in their study, produced different azo dyestuffs. These azo dyestuffs has been used to increase the durability of materials in textile, paper, plastic, leather, cosmetics, ink and various fields. In addition dyestuff complexes have also been used in advanced technology areas such as biomedical research, advanced applications in organic synthesis, ink-jet printers, photocopying, liquid crystal, thermal transfer printing dyestuffs.

Hsieh (1990) and Wang(1991) in their study used to o,o'-dihydroxyazo dyestuffs and used to chromium and cobalt metal complexes in the field of electrophotography. They determined that they have good washing and light fastness properties on protein and polyamide fibers.

Beffa (1984) in this study, o,o'-dihydroxyazo and metal complex dyestuffs have been used to dyeing and printing natural fibers and synthetic polyamide fibers.

Saad et al.(1996) in their study, determined that dihydroxynaphthalene derived azo compounds were used as color modifiers for diacetate and polyester fibers.

Szymczyk et al.(2004) in their study, identified that alumium complexes containing o-hydroxy-o'-carboxyazo ligand can be used instead of heavy metal complexes.

James and Hockessin(1975) in their study, synthesized disazo cationic dyestuffs containing two quaternary ammonium groups. They dyed acid modified nylon fibers in the pH 4-7 range with synthesized dyestuffs. They observed that dye uptake, light and wet fastness were good.

Stingelin and Reinach (1993) in their study, synthesized cationic azo dyestuffs. They are used azo compounds for printing and dyeing materials such as paper and leather. In addition, acid modified polyesters, polyamides, acrylonitrile copolymers and homopolymers were dyed with synthesized azo compounds. They found that fastness values (light fastness, acid and alkali fastness, etc.) were good. In addition, they observed that the affinity of the synthesized azo compounds to textile material was very good.

Gorgani and Taylor (2006) in their study, synthesized soluble reactive dyestuffs containing one or two cationic groups and dyed the polyamide fiber. They investigated the effect of pH on dyeing performance. In addition, washing fastness of the fabrics dyed with these dyestuffs was checked and it was observed that the polyamide fiber had a good fastness.

2. Effects of Heavy Metals Used in Coloration Textile Materials on Human Health

The most important mordant dyestuffs are natural dyestuffs. Their chromophore group is alizarin. The aromatic structure of the dissolved Alizarin Red dyestuff is resistant to degradation. It is dangerous for the aqua ecosystem and human health. The removal of Alizarin Red(AR) from water many methods such as photocatalytic degradation (Jabeen et al.,2017), adsorption (Fayazi et al.,2015) and electrochemical degradation (Zhu et al.,2018) are applied. Most of the mordant dyestuffs consist of

heavy metal salts such as aluminium, iron, copper, tin and chromium. Metal salts such as copper sulfate and potassium bichromate are not used today due to their toxicity. The use of tin at a certain concentration is allowed. Compounds such as potassium aluminium sulfate, aluminium sulfate, aluminium acetate and iron sulfate are ecologically preferred metal mordants. However, they should be used in minimum amounts. The use of some metals and chemicals are not completely prohibited, but must be within certain limits according to the ecological criteria in Oekotex standards (İşmal, E.,2019). Table 1 indicates typical ecological aspects of different dyestuff classes (Kohla, 2008).

Dyestuff	Ecological Aspects		
Group	Heavy Metal	AOX	Other
Reactive	[r] Cu(structurally bound, eg phthalocyanine blue)	[o] permanent in the chromophore and hydrolyzable)	[f] high salt content
Direkt	[r] Cu(structurally bound, eg phthalocyanine blue)	[n]	High salt content, post treatment for fastnmess improvement
1:1/1:2 Metal	[f] Cr, Co, Cu (structural	[n]	Significant organic
Complex	bond)		strain
Pigment	[r] Cu(structurally bound, eg phthalocyanine blue)	[r] 1-15% Cl (at 30% of all pigments)	No final rinse, formaldehyde and methanol possible

 Table 1. Typical ecological aspects of different dyestuff classes (Kohla, 2008)

Metal-based complex dyestuffs give chromium to natural water resources. This chromium is carcinogenic (Anklier, 1981).

Heavy metals are also used in the manufacture of some dyestuffs and pigments. In addition, metals can contaminate to textile products through dyeing and finishing processes (Freedman, 1995).

Limit values of extractable heavy metals are based on threshold limit values. In other words, higher concentrations of heavy metals than drinking water are not allowed on the surface of the skin in contact with the textile material. The human body tends to discharge perspiratory rather than absorb it. There is no toxicological situation for very low levels of extractable heavy metals for eco-textiles (Material Safety Data Sheet Lead MSDS,2017).

Heavy metals affect the system operation in the human body. These systems are blood and circulatory systems, toxin removal systems (intestines, liver, renals, skin), hormonal system, energy production systems, enzymes, stomach, immune, nervous and production systems and urinary system. Heavy metals can cause allergic reactions, death of harmful bacteria and beneficial bacteria and tissue damage (Siegel, 2002). The systems that the effective of heavy metals and their harmful are shown in Table 2 (Siegel, 2002).

Heavy Metals	System/Organ	Heavy Metal Effect	
Hg	Central nervous system	Brain damage	
Pb^{+2}		Decreased neurological functions	
Cd	Kidney	Clomerular destruction	
Hg, As	Production systems	Miscarriage	
Pb	Blood circulation	Decreased blood cell	
Cd		Mild anemia(blood deficiency)	
As		Anemia	
Cd	Respiratory Systems	Emphysema	
As		Increased fibrous connective	
Hg		Tissue between cells	
Se		Brongitis effects	
Zn		Respiratory tract inflammation	
Cu		Acute poisonings	
Hg	Brain	Deformation	
Cu			
As	Liver	Cirrhosis	
Cd	Lung	Cancer	
As	Cancer	Cancer	
Cd	Skeleton	Osteomolosis	
Se		Tooth decay	
Zn		Adele, articular pain	
Cd, As	Kromozom	Chromosomal fault	

 Table 2. The systems that the effective of heavy metals and their harmful (Siegel, 2002).

Lead and cadmium cause irritation on the skin, it can also damage the liver, kidney and nervous system (Seventekin vd.,1998).

In addition, mercury can cause growth retardation, vitamin D metabolism disorders and inhibition of hemoglobin synthesis. Depending on the sensitivity of the skin in contact with chromium, it can cause ulcer formation (E.Örün, 2015).

And also, arsenic and mercury have very high toxic properties. As a result the negative properties of heavy metals are toxic, they influence the nervous system, cause cancer, cause skin irritation and allergic reactions (Mohan vd., 2007).

3.Conclusion and Recommendations

Dyestuff gives a chemical or physicochemical reaction with the surface of the textile material.

In this study; heavy metal-based dyestuffs used in the coloration of textile materials, their chemical structures, properties, areas of usage and their effects on human health were examined.

There heavy metals such arsenic(As), are as cobalt(Co). chromium(Cr), cadmium (Cd). copper(Cu), nickel(Ni).lead(Pb),zinc(Zn),aluminium(Al),mercury(Hg) and iron(Fe) in the structure of the dvestuffs used in the coloration of textile products. These metals are mainly found in the structures of mordant, metal complex, metal complex carbonyl, o,o'-dihydroxyazo, hydroxy nitroso,Cuphthalocvanine, cube, chromium complex and solvent dvestuffs.

Heavy metals in dyestuffs have two important properties. The first heavy metals are used as catalysts during the production of dyestuffs. The second; heavy metals form a chelate(complex) compound with dyestuff molecules.

As a result, the concentrations of the heavy metals in the dyestuffs must be in the range of certain values (ppm) so that they are not toxic, do not affect the nervous system, do not cause cancer and allergic reactions. These values are also given in Table 3(Chavan vd.,2011).

Heavy Metals	Typical concentration(ppm)	Dyestuffs containing heavy metal	
Arsenic(As)	< 1-1.4	Reactive Dyestuffs	
Cadmium(Cd)	< 1	All dyestuff classes	
Chromium(Cr)	3-83	Vat dyestuffs	
Cobalt (Co)	< 1-3.2	Acid dyestuffs	
Copper(Cu)	33-110	Vat dyestuffs	
Lead (Pb)	6-52	Reactive dyestuffs	
Mercury (Hg)	0.15-1	Vat dyestuffs	
Zinc (Zn)	3-32	Basic dyestuffs	

 Table 3. Concentrations of heavy metals in the dyestuff molecule (Chavan vd., 2011)

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<u>Chapter 4</u>

6

FRACTIONAL ORDER PD CONTROLLER DESIGN USING SUBSTITUTIONS OF TIME DELAY¹

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1. INTRODUCTION

Time delay is one of the issues that has been studied for years. And, stability analysis of such systems is an important topic in control theory. There are delays in many practical systems such as chemical and biological processes, communication systems, electrical networks, control systems, etc. (S. Pakzad & Pakzad, 2011). In fact, these systems are of uncertain nature, and they can make the system unstable (Loiseau, Michiels, Niculescu, & Sipahi, 2009). Since this term is not linear, it makes it difficult to find the roots of the characteristic equation and to analyze the stability of the system (Naveed, Sönmez, & Ayasun, 2019).

One of the popular research topics today is fractional-order systems (FOS). However, studying such systems is mathematically difficult. In such systems, the analysis becomes even more complex when time delay is involved. It is possible to control FOS using both integer-order and fractional-order controllers (FOC). However, it has been observed that FOC provide better results for the control of FOS (Chen, Petráš, & Xue, 2009). Fractional-order controllers offer a more flexible structure as they have extra tuning parameters than the conventional integer-order controllers. FOS can appear in many fields, including applied science and engineering. The fractional-order proportional derivative (FOPD) controller is a special case of the fractional-order PID (FOPID) controller when $\lambda = 0$ in $PI^{\lambda}D^{\mu}$ ($PI^{\lambda}D^{\mu}$ is one another representation of a FOPID controller in the literature). It is clear from here that fractional-order PI (FOPI) is obtained when $\mu = 0$ and classical PID controller is obtained when both are equal to one. If both parameters are zero, a proportional controller is obtained.

When we look at the literature, it is seen that the Euler expansion, that is $e^{-\tau j\omega} = \cos(\omega \tau) - j\sin(\omega \tau)$, is mostly used for the time delay term in obtaining the equations. The problem here is that the time delay term can not be introduced as an independent element in the Euler expansion, which creates difficulties in the stability analysis (Hua, Liu, & Guan, 2014). Various approximation and/or transformations are used to overcome this difficulty created by the term time delay. The most common of these methods is the Padé approximation. Since the equations related to the Padé approximation are widely known, they will not be given separately here. Other transformations used instead of the term time delay are the Rekasius and Thowsen substitutions. However, the studies in the literature that apply Rekasius and Thowsen substitutions to FOS are very limited. Besides, stability analysis in fractional-order time delay systems is more complex than integer-order systems. Applying these substitutions to FOS imposes a serious mathematical load. The aim of this study is to reduce the characteristic equations with infinite number of solutions to finite polynomial equations and reach a finite number of solutions by using Rekasius and Thowsen substitutions. Thus, fractional-order PD parameters are obtained using these substitutions.

Some important studies on the Rekasius transformation are available in (Fazelinia, Sipahi, & Olgac, 2007; Gündüz, Ayasun, & Sönmez, 2019; Jia, Cao, Yu, & Zhang, 2007; Olgac & Sipahi, 2004; Sönmez & Ayasun, 2019). In (Gündüz et al., 2019), stability analysis of time delay microgrid systems was performed. In (Fazelinia et al., 2007), stability robustness analysis of systems with multiple time delays was made with the concept of "building block". In (Jia et al., 2007), a simple approach is proposed to determine the delay margin in the power system. (Olgac & Sipahi, 2004) presents a method for the stability of neutral type linear time invariant time delay systems. In (Sönmez & Ayasun, 2019), a study was conducted to calculate the maximum time delay of the time delay generator excitation control system using the Rekasius method. The point to note here is that these transformations are not just an approximation, but the exact expression of the time delay term for $s = \mp i\omega$ (M. A. Pakzad & Pakzad, 2017). Since the Thowsen transform is a more complex substitution, studies on this are very few in the literature.

Rekasius substitution is a bilinear transformation that calculates imaginary roots algebraicly. It is defined by Eq. (1) (Rekasius, Z., 1980).

$$e^{-\tau s} = \frac{1 - Ts}{1 + Ts}, \ \tau \in \mathbb{R}^+, \ T \in \mathbb{R}$$
(1)

This representation is valid for $s = j\omega$, $\omega \in R$, where the value of *T* is called pseudo-delay. Here, we can say that the Rekasius substitution is equivalent to the first-order Padé approximation for $\tau = 2T$. The relationship between τ and *T* can be explained by Eq. (2).

$$\tau = \frac{2}{\omega} \Big(\tan^{-1}(\omega T) \mp \ell \,\pi \Big), \, 0 \le \tan^{-1}(.) < \pi, \, \ell = 0, 1, 2, \dots$$
(2)

Where, T is obtained as follows.

$$T = \frac{1}{\omega} \tan\left(\frac{\tau\omega}{2} \mp \ell \pi\right), \ \ell = 0, 1, 2, \dots$$
(3)

Eq. (3) is valid for $\tau \omega / 2 \mp \ell \pi \neq \pi / 2$. To avoid imaginary zeros in τ values, $T \rightarrow \infty$ or $e^{-\tau s} = -1$ conditions must be considered. (Hertz, Jury, & Zeheb, 1984). Because Eq. (1) is only valid for $e^{-j\omega \tau} \neq -1$.

The advantages of using the Rekasius substitution can be summarized as follows (Gu, Chen, & Kharitonov, 2003; Gündüz et al., 2019).

1. Converts the characteristic equation to a simple polynomial without exponential terms.

2. It effectively reduces the analysis of stability problem in time delay systems.

3. It performs the stability analysis by calculating roots on the real axis.

4. It allows the application of classical stability criterions such as the Routh-Hurwitz and the root locus.

Thowsen, considering a more complex Routh-Hurwitz analysis instead of the Rekasius transformation, suggested using Eq. (4) in which the full circle passes (MacDonald, 1985). Therefore, $e^{-\tau j\omega}$ point is defined by Eq. (4) for some $T \in [0, \infty)$ values (Thowsen, 1981).

$$e^{-\tau s} = \left[\frac{1-Ts}{1+Ts}\right]^2 = \frac{1-2Ts+T^2s^2}{1+2Ts+T^2s^2}$$
(4)

2. FOPD CONTROLLER DESIGN USING STABILITY REGION CONCEPT



Figure 1. A control system with unity feedback

Consider a unity feedback control system shown in Figure 1. Here, $G_p(s)$ is the controlled system and is defined by Eq. (5).

$$G_{p}(s) = G(s)e^{-\tau s} = \frac{N(s)}{D(s)}e^{-\tau s}$$
(5)

C(s) is the controller that stabilizes the system and is expressed by Eq. (6).

$$C(s) = k_p + k_d s^\mu \tag{6}$$

In Eq (7), $\Delta(s)$ is the characteristic equation of the system. Substituting

 $G_p(s)$ and C(s) in the general form for this system, the characteristic equation can be obtained as follows.

$$\Delta(s) = 1 + C(s)G_p(s) = D(s) + (k_p + k_d s^{\mu})N(s)e^{-\tau s}$$
(7)

Where, Eq. (1) is used instead of the time delay term. If $s = j\omega$ is written after separating the numerator and denominator polynomials of G(s) in Eq. (5) as N(s) and D(s), decomposing these polynomials into even and odd parts one obtains Eq. (8).

$$G(j\omega) = \frac{N_e(-\omega^2) + j\omega N_o(-\omega^2)}{D_e(-\omega^2) + j\omega D_o(-\omega^2)}$$
(8)

For the simplicity, $(-\omega^2)$ will not be used in the remainder of the paper. Using Eq. (9), we can divide the closed-loop characteristic equation into real and imaginary parts as in Eq. (10).

$$(j\omega)^{\lambda} = \omega^{\lambda} (\cos\frac{\pi}{2}\lambda + j\sin\frac{\pi}{2}\lambda)$$

$$(9)$$

$$\Delta(j\omega) = D_{e} - \omega^{2}TD_{o} + k_{p}N_{e} + \omega^{2}Tk_{p}N_{o} + \omega^{\mu}\cos(\frac{\pi}{2}\mu)k_{d}N_{e}$$

$$-\omega^{(\mu+1)}\cos(\frac{\pi}{2}(\mu+1))Tk_{d}N_{e} + \omega^{(\mu+1)}\cos(\frac{\pi}{2}(\mu+1))k_{d}N_{o}$$

$$-\omega^{(\mu+2)}\cos(\frac{\pi}{2}(\mu+2))Tk_{d}N_{o} + j[\omega TD_{e} + \omega D_{o} - \omega Tk_{p}N_{e} + \omega k_{p}N_{o}$$

$$(10)$$

$$+\omega^{\mu}\sin(\frac{\pi}{2}\mu)k_{d}N_{e} - \omega^{(\mu+1)}\sin(\frac{\pi}{2}(\mu+1))Tk_{d}N_{e}$$

$$+\omega^{(\mu+1)}\sin(\frac{\pi}{2}(\mu+1))k_{d}N_{o} - \omega^{(\mu+2)}\sin(\frac{\pi}{2}(\mu+2))Tk_{d}N_{o}]$$

If we set the real and imaginary parts of $\Delta(j\omega)$ to zero, Eq. (11) is obtained.

$$\Delta(j\omega) = \operatorname{Re}_{\Delta} + j\operatorname{Im}_{\Delta} = 0 \tag{11}$$

Accordingly, the real part is obtained in Eq. (12), and the imaginary part is obtained in Eq. (13).

$$k_{p}[N_{e} + \omega^{2}TN_{o}] + k_{d}[\omega^{\mu}\cos(\frac{\pi}{2}\mu)N_{e} - \omega^{(\mu+1)}\cos(\frac{\pi}{2}(\mu+1))TN_{e} + \omega^{(\mu+1)}\cos(\frac{\pi}{2}(\mu+1))N_{o} - \omega^{(\mu+2)}\cos(\frac{\pi}{2}(\mu+2))TN_{o}] = -D_{e} + \omega^{2}TD_{o}$$
(12)

$$k_{p}[-\omega TN_{e} + \omega N_{o}] + k_{d}[\omega^{\mu}\sin(\frac{\pi}{2}\mu)N_{e} - \omega^{(\mu+1)}\sin(\frac{\pi}{2}(\mu+1))TN_{e} + \omega^{(\mu+1)}\sin(\frac{\pi}{2}(\mu+1))N_{o} - \omega^{(\mu+2)}\sin(\frac{\pi}{2}(\mu+2))TN_{o}] = -\omega TD_{e} - \omega D_{o}$$
(13)

If Eqs. (12) and (13) are rearranged following equations are obtained.

$$k_p C_1(\omega) + k_d C_2(\omega) = C_3(\omega) \tag{14}$$

$$k_p D_1(\omega) + k_d D_2(\omega) = D_3(\omega)$$
⁽¹⁵⁾

Accordingly, the coefficients are as follows.

$$C_1(\omega) = N_e + \omega^2 T N_o \tag{16}$$

$$C_{2}(\omega) = \omega^{\mu} \cos(\frac{\pi}{2}\mu)N_{e} - \omega^{(\mu+1)}\cos(\frac{\pi}{2}(\mu+1))TN_{e}$$
(17)

$$+\omega^{(\mu+1)}\cos(\frac{\pi}{2}(\mu+1))N_{o} - \omega^{(\mu+2)}\cos(\frac{\pi}{2}(\mu+2))TN_{o}$$

$$C_3(\omega) = -D_e + \omega^2 T D_o \tag{18}$$

$$D_1(\omega) = -\omega T N_e + \omega N_o \tag{19}$$

$$D_2(\omega) = \omega^{\mu} \sin(\frac{\pi}{2}\mu) N_e - \omega^{(\mu+1)} \sin(\frac{\pi}{2}(\mu+1)) T N_e$$
(20)

$$+\omega^{(\mu+1)}\sin(\frac{\pi}{2}(\mu+1))N_{o} - \omega^{(\mu+2)}\sin(\frac{\pi}{2}(\mu+2))TN_{o}$$

$$D_3(\omega) = -\omega T D_e - \omega D_o \tag{21}$$

 k_p and k_d terms are obtained by Eqs. (22) and (23). The stability boundary locus in the (k_p, k_d) plane can be obtained using these equations (in this process, complex root boundary, real root boundary and infinite root boundary must be investigated. Necessary details can be found in (Serdar E. Hamamci, 2008; Serdar Ethem Hamamci & Tan, 2006; Tan & Atherton, 2006).

$$k_p = \frac{C_3(\omega)D_2(\omega) - D_3(\omega)C_2(\omega)}{C_1(\omega)D_2(\omega) - D_1(\omega)C_2(\omega)}$$
(22)

$$k_d = \frac{C_1(\omega)D_3(\omega) - D_1(\omega)C_3(\omega)}{C_1(\omega)D_2(\omega) - D_1(\omega)C_2(\omega)}$$
(23)

The same procedure is repeated for the Thowsen transform, this time using Eq. (4). The resulting equations are given below.

The characteristic equation is obtained as follows.

$$\Delta(j\omega) = D_{e} - 2\omega^{2}TD_{o} - \omega^{2}T^{2}D_{e} + k_{p}N_{e} + 2\omega^{2}Tk_{p}N_{o} - \omega^{2}T^{2}k_{p}N_{e}$$

$$+\omega^{\mu}\cos(\frac{\pi}{2}\mu)k_{d}N_{e} + \omega^{(\mu+1)}\cos(\frac{\pi}{2}(\mu+1))k_{d}N_{o}$$

$$-2\omega^{(\mu+1)}\cos(\frac{\pi}{2}(\mu+1))Tk_{d}N_{e} - 2\omega^{(\mu+2)}\cos(\frac{\pi}{2}(\mu+2))Tk_{d}N_{o}$$

$$+\omega^{(\mu+2)}\cos(\frac{\pi}{2}(\mu+2))T^{2}k_{d}N_{e} + \omega^{(\mu+3)}\cos(\frac{\pi}{2}(\mu+3))T^{2}k_{d}N_{o}$$

$$+j[\omega D_{o} + 2\omega TD_{e} - \omega^{3}T^{2}D_{o} + \omega k_{p}N_{o} - 2\omega Tk_{p}N_{e} - \omega^{3}T^{2}k_{p}N_{o}$$

$$+\omega^{\mu}\sin(\frac{\pi}{2}\mu)k_{d}N_{e} + \omega^{(\mu+1)}\sin(\frac{\pi}{2}(\mu+1))k_{d}N_{o}$$

$$-2\omega^{(\mu+1)}\sin(\frac{\pi}{2}(\mu+1))Tk_{d}N_{e} - 2\omega^{(\mu+2)}\sin(\frac{\pi}{2}(\mu+2))Tk_{d}N_{o}$$

$$+\omega^{(\mu+2)}\sin(\frac{\pi}{2}(\mu+2))T^{2}k_{d}N_{e} + \omega^{(\mu+3)}\sin(\frac{\pi}{2}(\mu+3))T^{2}k_{d}N_{o}]$$
(24)

The real and imaginary parts of $\Delta(j\omega)$ are given as follows.

$$k_{p}[N_{e} + 2\omega^{2}TN_{o} - \omega^{2}T^{2}N_{e}] + k_{d}[\omega^{\mu}\cos(\frac{\pi}{2}\mu)N_{e} + \omega^{(\mu+1)}\cos(\frac{\pi}{2}(\mu+1))N_{o} - 2\omega^{(\mu+1)}\cos(\frac{\pi}{2}(\mu+1))TN_{e} - 2\omega^{(\mu+2)}\cos(\frac{\pi}{2}(\mu+2))TN_{o} + \omega^{(\mu+2)}\cos(\frac{\pi}{2}(\mu+2))T^{2}N_{e} + \omega^{(\mu+3)}\cos(\frac{\pi}{2}(\mu+3))T^{2}N_{o}] = -D_{e} + 2\omega^{2}TD_{o} + \omega^{2}T^{2}D_{e} + \omega^{(\mu+3)}\sin(\frac{\pi}{2}(\mu+3))T^{2}N_{o}] + k_{d}[\omega^{\mu}\sin(\frac{\pi}{2}\mu)N_{e} + \omega^{(\mu+1)}\sin(\frac{\pi}{2}(\mu+1))N_{o} - 2\omega^{(\mu+1)}\sin(\frac{\pi}{2}(\mu+1))TN_{e} - 2\omega^{(\mu+2)}\sin(\frac{\pi}{2}(\mu+2))T^{2}N_{e} + \omega^{(\mu+3)}\sin(\frac{\pi}{2}(\mu+3))T^{2}N_{o}] = -\omega D_{o} - 2\omega TD_{e} + \omega^{3}T^{2}D_{o}$$
(26)

Using Eqs. (25) and (26), one obtains Eqs. (14) and (15) again. And coefficients are as follows.

$$C_1(\omega) = N_e + 2\omega^2 T N_o - \omega^2 T^2 N_e$$
⁽²⁷⁾

$$C_{2}(\omega) = \omega^{\mu} \cos(\frac{\pi}{2}\mu)N_{e} + \omega^{(\mu+1)}\cos(\frac{\pi}{2}(\mu+1))N_{o}$$
$$-2\omega^{(\mu+1)}\cos(\frac{\pi}{2}(\mu+1))TN_{e} - 2\omega^{(\mu+2)}\cos(\frac{\pi}{2}(\mu+2))TN_{o}$$
(28)

$$+\omega^{(\mu+2)}\cos(\frac{\pi}{2}(\mu+2))T^2N_e + \omega^{(\mu+3)}\cos(\frac{\pi}{2}(\mu+3))T^2N_o$$

$$C_{\mu}(\mu) = D_{\mu} + 2\mu^2 T D_{\mu} + \mu^2 T^2 D_{\mu}$$
(20)

$$C_3(\omega) = -D_e + 2\omega^2 T D_o + \omega^2 T^2 D_e$$
⁽²⁹⁾

$$D_1(\omega) = \omega N_o - 2\omega T N_e - \omega^3 T^2 N_o$$
(30)

$$D_{2}(\omega) = \omega^{\mu} \sin(\frac{\pi}{2}\mu)N_{e} + \omega^{(\mu+1)}\sin(\frac{\pi}{2}(\mu+1))N_{o}$$

$$-2\omega^{(\mu+1)}\sin(\frac{\pi}{2}(\mu+1))TN_{e} - 2\omega^{(\mu+2)}\sin(\frac{\pi}{2}(\mu+2))TN_{o}$$

$$+\omega^{(\mu+2)}\sin(\frac{\pi}{2}(\mu+2))T^{2}N_{e} + \omega^{(\mu+3)}\sin(\frac{\pi}{2}(\mu+3))T^{2}N_{o}$$
(31)

3. A TUNING METHOD FOR FOPD CONTROLLERS

In this section, a design method for the FOPD controller is aimed. This method was introduced to the literature by Onat (Onat, 2019) and is known as the convex stability region (CSR). It is first applied to PI-PD controller structure by Onat.

Let's assume that the stability region curve of the FOPD controller providing stability for the system given in Figure 1 is obtained as in Figure 2 for $\mu = 0.99$. The CSR is obtained by using the corner and cusp points of the stability boundary curve formed by the controller parameters (Onat, 2019; M. M. Ozyetkin, Bekiroglu, & Srinivasan, 2020). Cusp and corner points in (k_p,k_d) plane are ($\bar{k}_{p1},\bar{k}_{d1}$), ($\bar{k}_{p2},\bar{k}_{d2}$),...,($\bar{k}_{pf},\bar{k}_{pf}$), and ($\bar{\bar{k}}_{p1},\bar{\bar{k}}_{d1}$), ($\bar{\bar{k}}_{p2},\bar{\bar{k}}_{d2}$),...,($\bar{\bar{k}}_{pg},\bar{\bar{k}}_{dg}$), respectively (M. M. Ozyetkin, Bekiroglu, & Srinivasan, 2020). The number of cusp and corner points are represented by *f* and *g*, respectively. The centroid of the CSR of FOPD is calculated by Eqs. (33) and (34) (M. M. Ozyetkin et al., 2020).

$$k_{pc} = \frac{\sum_{i=1}^{n} \bar{k}_{pi} + \sum_{i=1}^{m} \bar{\bar{k}}_{pi}}{f + g}$$
(33)



Figure 2. Stability region and convex stability region for $\mu = 0.99$

4. SIMULATIONS

In this section, a numerical example is given for the comparison of the methods proposed in this paper. More details on the centroid of the CSR used for controller design in this paper can be found in (Onat, 2019; M. M. Ozyetkin, 2022; M. M. Ozyetkin et al., 2020). Besides, detailed information about the Weighted Geometrical Center (WGC) method which is used for the comparison can be found in (M. M. Ozyetkin, 2018; M. M. Ozyetkin, Onat, & Tan, 2018; M. M. Ozyetkin, Onat, & Tan, 2020).

4.1. Example

Consider a FOS (M. M. Ozyetkin & Tan, 2017) given by Eq. (35) for the control system shown in Figure 1.

$$G_p(s) = \frac{1}{s^{1.9} + s} e^{-s} = \frac{1}{s(s^{0.9} + 1)} e^{-s}$$
(35)

The purpose of this example is to calculate FOPD controller parameters using the centroid of the CSR for the control system defined by Eq. (35). Here, the centroid of the CSR and the WGC points are calculated and the step responses of them are compared. Let us first consider the 10^{th} order approximation of $s^{0.9}$, which is obtained by the continued fraction expansion (CFE) method (Astekin & Özyetkin, 2021).

$$680.37s^{10} + 32586.49s^{9} + 409578.54s^{8} +$$

$$1988381.33s^{7} + 4331830.76s^{6} + 4493356.65s^{5} +$$

$$s^{0.9} \approx \frac{2224971.29s^{4} + 498908.57s^{3} + 44145s^{2} + 1090s + 1}{s^{10} + 1090s^{9} + 44145s^{8} + 498908.57s^{7} +$$

$$2224971.29s^{6} + 4493356.65s^{5} + 4331830.76s^{4} +$$

$$1988381.33s^{3} + 409578.54s^{2} + 32586.49s + 680.37$$
(36)

If we separate the numerator and denominator polynomials of $G_p(s)$ in Eq. (35) as N(s) and D(s), and divide these polynomials into even (N_e, D_e) and odd (N_o, D_o) parts, and substitute $s = j\omega$ in this equation, the result is as follows.

$$N_{e} = -\omega^{10} + 44145\omega^{8} - 2224971.29\omega^{6} + 4331830.76\omega^{4} - 409578.54\omega^{2} + 680.37 N_{o} = 1090\omega^{8} - 498908.57\omega^{6} + 4493356.65\omega^{4} - 1988381.33\omega^{2} + 32586.49 D_{e} = -33676.49\omega^{10} + 2487289.9\omega^{8} - 8986713.3\omega^{6} + 2487289.9\omega^{4} - 33676.49\omega^{2} D_{o} = -681.37\omega^{10} + 453723.54\omega^{8} - 6556802.05\omega^{6} + 6556802.05\omega^{4} - 453723.54\omega^{2} + 681.37$$
(37)

First of all, the stability boundary locus for $\mu = 0.99$, the CSR and the centroid of the CSR are shown in Figure 2. Here, the centroid of the CSR for the FOPD controller is calculated according to (M. M. Ozyetkin et al., 2020). Table 1 demonstrates (k_p, k_d) values for different μ values. Stability regions, centroids and the WGC points for $\mu = 0.9$, $\mu = 1$ and $\mu = 1.1$ are shown in Figure 3. Figure 4 shows the stability regions for $\mu \in [0.1, 1.1]$ using Rekasius and Thowsen substitutions. Comparison of
the stability regions of the original system for $\mu = 0.5$ and for $\mu = 0.99$ using different methods is given in Figure 5. It is observed that the stability regions obtained using Rekasius and Thowsen substitutions exactly match the original system response. It has been seen that the second-order Padé approximation partially approximates the original system. Set point responses of $\mu = 0.9$, $\mu = 1$ and $\mu = 1.1$ for the WGC and for the centroid of the CSR methods are shown in Figure 6.

μ	k_{p}	k_d
0.1	0.93138	-0.24673
0.2	0.58136	0.23633
0.3	0.48036	0.47345
0.4	0.44411	0.64363
0.5	0.43947	0.77628
0.6	0.45458	0.88083
0.7	0.48381	0.95719
0.8	0.52635	0.99521
0.9	0.58675	0.97552
1	0.6637	0.85777
1.1	0.77106	0.5509

Table 1. (k_p, k_d) values for different values of μ



Figure 3. Stability regions, centroids and the WGC points for $\mu = 0.9$, $\mu = 1$ and $\mu = 1.1$



Figure 4. Stability regions for $\mu \in [0.1, 1.1]$ using Rekasius substitution



Figure 5. Comparison of the stability regions for $\mu = 0.5$ and $\mu = 0.99$



Figure 6. Comparison of unit step responses for $\mu = 0.9$, $\mu = 1$ and $\mu = 1.1$

5. CONCLUSION

In this study, it has been shown that Rekasius and Thowsen substitutions in obtaining stability regions gives very close results with the original system. Therefore, these substitutions can be easily used in order to eliminate the non-linear problem caused by time delay term in the characteristic equation. In addition, stability tests such as Routh can be applied to the system using these substitutions. However, although they provide the nearly same result, preferring the Rekasius substitution will provide simpler mathematical operations because it is simpler. Besides, Rekasius substitution was used to obtain the FOPD equations. A simple design method known as the centroid of CSR is proposed for the FOPD design and the FOPD parameters are calculated using this method. This method is based on the concept of the stability region in the plane formed by the controller parameters and the calculation of the centroid of the CSR. The advantages of the proposed method are that it calculates the controller parameters without the need for complex methods and ensures the stability of the closed-loop system. In future studies, stability regions for PI, PD, PID, FOPID, FOPI, etc. can be determined by using Rekasius and Thowsen substitutions. After obtaining the necessary equations for different controllers, the proposed design method can be applied to these systems. More extensive studies are needed on both Rekasius and Thowsen substitutions. As a result, there is a potential for many studies to emerge on these topics.

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1. INTRODUCTION

Special control methods are required for synchronization between the frequency of the drive source and the position of the rotor magnets in a permanent magnet synchronous motor. The vector control technique invented by Blaschke (1970) is also known as field oriented control (FOC). The magnetic flux is used to control the space vector of current and voltage [1]. In this technique, the stator current is decomposed into flux and torque generating components to achieve decoupled control of the PMSM driver, similar to a separately excited DC motor. Takahashi and Depenbrock (1980) invented the DTC scheme for the control of asynchronous motors, it has since become popular because of its simple control and easy implementation [2]. These two control techniques are widely used. For this reason, two control methods were examined in detail in this study.

2. CONTROL METHODS

Synchronous motors must be driven by a driver in order to operate at different speeds [3]. Control methods for electric motors are examined in two groups, depending on which parameters they control. Scalar control only controls magnitudes, while vector control controls both magnitudes and angles. Control methods are shown in Figure 2.1.



Figure 2.1.Permanent Magnet Synchronous Motor Control Methods

2.1. Scalar Control (V/f)

The simplest control method of the PMSM is scalar control, in which the relationship between voltage and frequency is kept constant throughout the motor speed range. The frequency is adjusted according to the desired synchronous speed and the magnitude of the voltage/current is adjusted to keep the ratio between them constant. No control over angles is used. This method uses an open-loop control approach without any feedback on the motor parameters and position. This method is preferred in applications such as pumps, fans and heating systems that do not require high performance [4].

2.2. Vector Control

It is possible to achieve higher dynamic performance in vector control with both magnitude and angle control of the flux compared to scalar control Vector control is divided into field oriented control and direct torque control [5].

2.2.1. Field oriented control (FOC)

In the field oriented control method, the stator current is divided into two components in order to control the magnetic flux and torque separately. In this control method, the i_d and i_q currents in the rotor rotating axes provide flux and torque control, respectively. When $L_d = L_q$ is taken for surface magnet synchronous motors in the torque equation, only i_q current is effective in torque control [6,8]. The schematic of the field oriented control method is shown in Figure 2.2.



Figure 2.2. Field Oriented Control Method Diagram of PMSM

In this method, the reference speed is compared with the speed information measured from the motor, the resulting error is applied to the PI control block and the desired i_{dref} and i_{qref} currents are obtained. These currents are passed through a PI process again and the V_{dref} and V_{qref} voltages required for the motor to rotate at the desired speed are obtained. These currents are passed through a PI process again to obtain the voltages V_{dref} and V_{qref} necessary for the motor to rotate at the desired speed. These two voltages are converted to the voltages V_{α} , V_{β} by the inverse Park transform. These voltages form the vector components of the pulse width modulation (PWM). In the pulse width modulation block, the signal is generated according to the voltages V_{α} , V_{β} . These signals are applied to the inverter as gate pulses. The voltages generated in the inverter are applied to the motor.

2.2.2. Direct torque control (DTC)

Flux and torque estimation is performed using stator current and voltage information of the motor. By comparing the speed of the motor and the reference speed, the resulting speed error is passed through the PI block and the reference torque is created. The error that occurs by comparing the reference moment with the estimated moment is transmitted to the hysteresis block. In the same way, the error caused by comparing the estimated flux with the reference flux is transmitted to the hysteresis block. The sectors are determined by the position information of the stator flux space vector [7,9,10]. According to the sector in which the flux vector is located, the appropriate voltage vector is selected from the defined switching table with the help of information obtained from the hysteresis block. Thus, the control process is carried out. The block diagram of direct torque control is shown in Figure 2.3.



Figure 2.3. Direct Torque Control Method Diagram of PMSM

3. SIMULATION OF FIELD-ORIENTED CONTROL IN PERMANENT MAGNET SYNCHRONOUS MOTOR WITH MATLAB/SIMULINK

The MATLAB/Simulink model of the FOC method of a permanent magnet synchronous motor is shown in Figure 3.1. By developing this model, simulation studies of auto-tuning PI controller, speed control and flux weakening control of FOC method were carried out on three models. FOC auto-tuning PI controller model is explained over model-1 shown in Figure 3.1.



Figure 3.1. MATLAB/ Simulink Model of the FOC Method of a Permanent Magnet Synchronous Motor (Model-1)

It is the system level model for implementing FOC control. The block on the left side contains the controller model, and the motor drive block on the right side contains the voltage supply and measurement of the PMSM. The motor drive block is shown in Figure 3.2.



Figure 3.2. Motor Drive Block

The measurement results taken from the output of the motor drive block are sent to the control block thanks to a delay block added to the feedback loop. The control block is shown in Figure 3.3.



Figure 3.3. Control Block

By comparing the ¹d, ¹q reference currents and real currents in the control block and with the help of the electrical angular speed (spd_we) information obtained from the mechanical angle of the rotor, the vd_reference and vq_reference voltages are generated with the PI and PID controllers in the current control block. By adding dynamic decoupling control terms to the output of the controllers, these reference voltages (V_{d_ref}, V_{q_ref}) necessary for the motor to rotate at the desired speed are generated. Decoupling control is necessary for designing linear current controls.

Afterwards, the rotor rotating axis set voltage components (V_d , V_q) are converted to the voltage values $V_{\alpha lpha}$, V_{beta} , which are the rotor fixed axis set components, by inverse Park transform. Then, these voltage components are converted into stator standing axis assembly (ABC) voltage components by inverse Clarke transform.

It was requested that the motor run continuously at 1000 rpm. The motor and controller parameters are set as shown in Table 3.1.

PMSM Motor Parameters		
Motor Power	18 kW	
Nominal Speed	1000 d/d	
d Axis Self Inductance (L _d)	1.7e-3 H	
q Axis Self Inductance (L _a)	3.2e-3 H	
Stator Resistance (R_s)	0.02 Ω	
Permanent Magnet Flux (λ_{m})	0.2205 W _b	
Number of Double Poles	4	
Controller Parameters		
d Axis Reference Current	100	

Table 3.1. Model-1 Falameter	Fable	3.1.	Model-1	Parameters
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q Axis Reference Current	-50
Gain P	1
Gain I	1

The designed model was run by adjusting the parameters. The scope image obtained after the simulation is completed is given in Figure 3.4 below.



Figure 3.4. The scope image

Here the ^{iq} reference current and its response are shown. It has been observed that there are overshoots in some places and the current does not reach steady state within three seconds of simulation time. When the controller parameters are initialized, the default proportional and integral gains are not optimal. Proportional and integral gains need to be adjusted to achieve better performance. Thanks to Simulink design optimization, PI controller gains can be adjusted automatically.

It is shown in Figure 3.5 that the iq current response follows the reference speed after the design is optimized.



Figure 3.5. The result of the simulation after the design optimization is performed

A speed control model (model-2) of the permanent magnet synchronous motor is obtained by adding a speed loop on top of the control loop in Model 1 and is shown in Figure 3.6.

FOC Control of PMSM

Figure 3.6. FOC speed control model (Model-2)

Since the only current producing torque here is the q axis current (i_q), the d axis current (i_d) is always equal to zero. Thanks to the current control, the torque angle is always $\delta = 90^{\circ}$ by taking $i_d = 0$. The internal structure of the control block is shown in Figure 3.7.



Figure 3.7. Control block

The electrical angular velocity (spd_we) information obtained from the mechanical angel of the rotor is converted into rpm speed unit with the help of the gain block. With the help of this information and the signal it receives from the speed command, i_d and i_q reference currents are generated by the PI process in the speed control block. Unlike Model 1, here the i_d and i_q reference currents are obtained from the speed control block.

The motor parameters are the same as model-1 and current and speed loop PI controller parameters are set as shown in Table 3.2.

Current Loop PI Controller Parameters				
Gain P	7.74			
Gain I	26.84			
Speed Loop PI Controller Parameters				
Speed Gain P	0.1			
Speed Gain I	0.1			

Table 3.2. Model-2 Parameters

Figure 3.8 where the speed follows the speed command when the simulation is performed. and it was observed at 3.9.



Figure 3.8. The speed command signal Figure 3.9. Scope image of the speed change

Flux weakening control is a very important issue for permanent magnet synchronous motor (PMSM). A given power inverter cannot operate PMSMs at high speeds because back emf is proportional to motor speed and airgap flow, resulting in higher back emf values. When the back emf becomes greater than the maximum output voltage of the drive, the PMSM cannot draw current and therefore can't generate torque. Therefore, when the opposite emf reaches the voltage threshold of a drive, the rotor speed of such an motor can't be increased unless the airgap flux is weakined. An extended speed range is achieved by the flux weaking control.

There are basically three situations when choosing flux weakening operating conditions. The first is when the speed is below the base speed, the second is when the speed is above the base speed and the attainable torque, and the last is when the speed is above the base speed and the torque can't be obtained.

In the first case, the speed is 600 rpm. The base speed for this motor is 876 rpm. In the case where the speed is below the base speed, no flux weaking control is actually performed. The speed torque curve for the PMSM operating at 600 rpm is shown in Figure 3.10. Here, the curve that is ellipse-shaped in light blue is the speed limit curve. The line shown in red is the MTPA line, which means the maximum torque per ampere. There are two torque commands, one 180 N.m and another 50 N.m, shown in dark blue. Both are intersected by the MTPA line. The intersections between the torque curve below base speed and the MTPA line are the most efficient operating points for this motor. So here point A and point B are optimized operating points.

In the second case, the speed is 1300 rpm. As the speed increases, the speed limit ellipse shrinks and only points located above or inside the speed limit curve can be reached. In this case, it is shown in Figure 3.11 that the 180 N.m torque curve intersects the MTPA line outside the speed limit ellipse and therefore this point is not reachable. In this case, point B should be chosen as the optimal operating point where the torque curve and the speed limit ellipse intersect. Because this is the operating point that can achieve the required torque while producing minimum loss. Since point A in the 50 N.m torque curve is still within this speed limit curve, this point continues to be used as the most appropriate operating point.

In the third case, the speed is 2500 rpm. The speed is above the nominal speed, and the torque cannot be obtained. As can be clearly seen in Figure 3.12, the 180 N.m torque curve does not intersect the speed limit ellipse and in this case this torque can't be obtained. Point B will be put in the lookup table because point B is the intersection of the speed limit curve and the MTPV line, which indicates the maximum torque that can be obtained under this speed limit. At point A, this torque is also obtained

because the 50 N.m torque curve intersects with the speed limit ellipse.



Figure 3.10. A Graphic of the state where the **Figure 3.11.** A graphic of the state where the speed is below the base speed above the base speed speed is above the base speed speed is above the base speed speed is above the base speed speed is above the base speed spe



Figure 3.12. A Graphic of the state where the speed 1s above the nominal speed

Finally looking at all the torque curves and speed limit ellipses, the final flux lookup table points are shown in Figure 3.13.



Figure 3.13. A graphic of lookup table

By adding a torque command to the control loop in Model 1, the flux weakening control model (model-3) of the permanent magnet synchronous motor is obtained and is shown in Figure 3.14.



Figure 3.14. FOC flux weakening control model (Model-3)

The motor parameters, current loop PI controller parameters and flux weakening lookup table data for the fluxweakening control model are set as shown in Table 3.3.

PMSM Motor Parameters		
Nominal Speed	876 d/d	
Selected Speed in the First Case	600 d/d	
Selected Speed in the Second Case	1300 d/d	
Selected Speed in the Third Case	2500 d/d	
Current Loop PI Controller Parameters		
Gain P	7.74	
Gain I	26.84	

Table 3.3. Model-3 Parameters.

In the control block, unlike model 1, the i_d and i_q reference currents are obtained from the flux weakening control block. The internal structure of the control block is shown in Figure 3.15.



Figure 3.15. Control Block

In the flux weakening control block, the speed (speed_rpm) is compared with the base speed (Param_BaseSpeed) and a speed error is generated. Then these three speed information is passed through the switch block. Here, the first input port to the switch is speed_rpm and the third input port is Param_BaseSpeed data ports. The second input port is the speed error control port. The criter for control port 2 are u2> = Threshold, u2> Threshold or u2 ~ = 0. The values obtained from here and the torque command (torque_command) create the lookup table to generate currents i_{d_ref} and i_{q_ref} . The lookup table surface is shown in Figure 3.16.



Figure 3.16. Lookup Table Surface

When the simulation is performed, it is observed in Figure 3.17 that the electromagnetic torque (Te) follows the torque command (torque_ cmd). In this graphic, it can be seen whether the motor is operating below or above the base speed, and the torque response has always followed the torque command.



Figure 3.17. Scope image of the flux weakening control model

A comparison of the three circuit models of the permanent magnet synchronous motor according to the FOC method is given below in Table 3.4.

MODEL	ADVANTAGE	DISADVANTAGE
FOC MODEL-1 Automatic Tuned PI Controller	* Due to PI controller design optimisation, PI gain coefficients are tuned automatically.	*If PI gain coefficient tunings are not made, current can't be reach to steady state value.
Model	* There is no need to external control block.* Easy to implement any kind of control system.	
FOC MODEL-2 Speed Control Model	 * Shows good visualization about closed loop speed control. * Easy to reach suitable or optimised results with speed command. 	*Have to use external speed control block.
FOC MODEL-3 Field Weakening Control Model	* According to torque command and base speed, easy to control the motor.	 * Have to implement external torque command. * According to attaching the field weakening block into the control circuit, motor control parameters are increased. * There is need to look up table for suitable flux values.

Table 3.4. Comparison of 3 FOC Models.

5. RESULTS AND DISCUSSIONS

Different from case studies in the literature, field oriented control strategy is implemented on three motor control models. These control models are, automatic tuned PI control model, speed control model and field weakening control model. According to enhance the simulation result in first model, proportional and integrator gains have been tuned. After the converting the PI coefficients about 10 times, optimisation has been converged.

Speed control of a PMSM has been achieved in second model. Different from the first model, d and q reference frame currents have been obtained from, speed control block. There has been a comparison between speed command and real rotor speed in speed control block. After the PI operation, q axis reference frame current has been obtained. This kind of control strategy is shows the closed loop speed control loop control.

Field weakening control model of a PMSM has been achieved in third model. Simulation result characteristics have been successfully showed that the operation speed of the PMSM, if under or above the motor base speed. During the control operation, torque answer has been followed the torque command forever. There has been lower number of motor control parameters in direct torque control method compared to the field oriented control strategy. Thus implementation problems of field oriented control model can be fixed with direct torque control strategy. Both of these control strategies can be improved and they can be used in field weakening control strategy.

In this study, measured motor control parameters have been transferred to the motor control block via closed loop control. Using of closed loop control strategy increases the control device cost. Thus it should be designed without sensors.

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Chapt	er 6

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INFLUENCE OF ZN COMPOSITION ON THERMAL, ELECTRICAL, MICROSTRUCTURE, AND CORROSION PROPERTIES OF SN-ZN ALLOYS

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1. Introduction

Pb and Pb-containing compounds are prohibited from using in European Union because of damaging the environment and human health. Most countries emphasize the limit of lead used in the industry for more appropriate development policies to protect the environment. In this context, significant efforts are made to develop lead-free alternative alloys instead of Pb-Sn eutectic solder alloy [1-3]. Physical and chemical requirements of lead-free solder alloy should be met economically and in other aspects. Sn-Zn eutectic alloy of lead-free solder alloy prominently provides electronic merge without modification. It is expected to be one of the best candidates to maintain the existing production line [1-9]. In addition, both micromechanical and metallurgical properties in terms of controlling the microstructure, strength, a casting alloy is complex in terms of silence and ductility. Thermal variables and their impact on the microstructure morphology depend on the heat transfer solidification conditions, which are affected by the temperature and composition. They have affected all the features directly [11-16]. There are studies related to the effect of temperature, Zn composition, microhardness, and used method; however, the electrical and thermal properties are rarely available in the literature. In this study, our purpose is to examine some physical properties and microhardness according to Zn composition, and the results are discussed.

2. Experimental Procedure

In the current work, the thermal conductivity variation according to composition and temperature were measured first by a radial heat flow apparatus for pure Sn, pure Zn, and Sn-1 wt. % Zn, Sn-9 wt. % Zn, Sn-14 wt. % Zn, Sn-50 wt. % Zn, Sn-80 wt. % Zn alloys. In the second step, the variations of electrical conductivity and resistivity values depending on the temperature and composition were determined from the Wiedemann-Franz law using the thermal conductivity values and their Lorenz coefficients. As the third, the fusion enthalpies (ΔH) and the specific heat capacity changes (ΔC_p) were determined via the DSC device. Finally, the materials' structural properties, surface morphologies, grain sizes, microhardness, and corrosion properties were investigated.

2.1. Sample Preparation and Measurement of the Thermal Conductivity

For various classes of materials having different ranges of thermal conductivity and temperature, various measurement methods are applied for the experimental determination of the thermal conductivity of materials [17-32]. The radial heat flow method is a well-known technique to measure solids' thermal conductivity. In this method, a sample in the form of a circular cylinder with a coaxial central hole, which contains either a

heater or a heat sink, is used [17]. This method was initially applied for measuring the thermal conductivity of solids for pure materials by Callendar and Nicolson [20], Niven [21], Powell [20], McElroy and Moore [22].

At the steady-state conditions, the thermal conductivity of a solid can be obtained by using Fourier's law with appropriate boundary conditions for the radial heat flow, and the temperature gradients are given as

$$\left(\frac{d}{d}\right)_{S} = -\frac{Q}{2\pi r\ell \kappa_{S}} \tag{1}$$

where κ_s is the thermal conductivity of the solid phase, Q is the total input power from the center of the sample, ℓ the length of the heating element, and r is the distance from the center. Integration of the Eq. (1) for the radial heat flow gives

$$\kappa_s = a_0 \frac{Q}{T_1 - T_2} \tag{2}$$

where a_0 is an experimental constant $(a_0 = h(f_2/r_1)/2\pi \ell)$, ℓ the length of the heating element, r_1 and r_2 fixed distances from the center of the sample $(r_2 > r_1)$, and T_1 , T_2 are the temperatures at the fixed positions r_1 and r_2 , respectively. Provided that the vertical temperature variation is zero or minimum, the thermal conductivity of the solid phase can be obtained via Eq. (2) by measuring the temperature difference between the two fixed points for a given power level. In the current work, the radial heat flow apparatus was chosen to obtain the thermal conductivity of solids due to its symmetrical characteristics. The details of experimental measurements, graphite crucible, and the radial heat flow apparatus was given in Refs. [20-32]. The thermal conductivity variation according to temperature and composition for pure Sn, pure Zn, and Sn-1 wt. % Zn, Sn-9 wt. % Zn, Sn-14 wt. % Zn, Sn-50 wt. % Zn, Sn-80 wt. % Zn alloys are shown in Fig. 1.



Fig. 1. Thermal conductivity vs. temperature and composition of Sn-(x) wt. % Zn (x= 1, 9, 14, 50, 80) alloys.

The temperature coefficients of the alloys were obtained from Eq.(3) for a given composition, the dependence of the thermal conductivity of solid-phase on temperature can be given as [33];

$$\alpha_{TTC} = \left(\frac{1}{\kappa_1}\right) \left(\frac{\Delta\kappa}{\Delta T}\right) \tag{3}$$

where κ_1 is the thermal conductivity at the initial temperature $T_{I_1} \alpha_{TTC}$ is the temperature coefficient of thermal conductivity vs. temperature between $\Delta T = T_2 - T_1$. $\Delta \kappa = \kappa_2 - \kappa_1$, κ_1 and κ_2 are the thermal conductivity at T_1 and T_2 , respectively. α_{TTC} can be obtained from thermal conductivity vs. temperature graph, given in Table 1.

2.2. Determination of the electrical conductivity and electrical resistivity

Electrical conductivity is influenced by substances' chemical composition and the stress state of crystalline structures. The electrical and thermal conductivity of metals and alloys in solid and liquid states is mainly carried by free electrons. Therefore, the Wiedemann-Franz-Lorenz law explains the relation between thermal conductivity and electrical resistivity [34, 35]:

$$\frac{\not{p}_{e}}{T} = \frac{\pi^{2}k^{2}}{3e^{2}} = L_{0}$$
(4)

where k is the Boltzman constant, e is the electron charge, and T is the absolute temperature. The constant

$$L_0 = \frac{\pi^2 k^2}{3e^2} = 2.445 x \mathbf{0}^{-8} W \Omega K^{-2}$$
(5)

is the Lorenz number. The Wiedemann-Franz law gives the relation between electrical conductivity and thermal conductivity as,

$$\sigma = \frac{\kappa_s}{I\!\!I} \tag{6}$$

where σ is electrical conductivity, κ_s thermal conductivity of the solid phase at temperature *T*, and *L* is the Lorenz number. This relationship is based on the fact that free electrons transport both the heat and electricity in the metals. In the current work, the variation of electrical conductivity according to temperature and composition was determined from the Wiedemann-Franz law by using S and L values. According to Eq. (6), the value of *L* seems to be constant and independent of the properties of materials. On the other hand, the value of *L* depends on the properties of materials in the literature. The values of *L* are well-known for pure materials, but they are unknown for alloys. To determine the variation of electrical conductivity according to temperature and the composition from the Wiedemann-Franz law, the value of *L* and κ_s . are required. The Lorenz numbers for pure Sn and pure Zn are 2.49×10⁻⁸ and 2.31×10⁻⁸ WΩ/K² [36], respectively.

$$L_{alloy} = \sum_{n=1}^{2} x_n L_n \tag{7}$$

Lorentz values for Sn-Zn binary alloys were calculated from Eq. (7). X_n is the percent by weight of the nth component; L_n is the percent of the Lorentz value's nth component. The electrical conductivities of Sn-Zn binary alloys according to temperature were determined using L_{alloy} and κ_s values. Electrical resistivity indicates how strongly a material impedes the flow of electric current, and it is an intrinsic, bulk (not thin-film) property of a material. Electrical resistivity is inversely proportional to electrical conductivity. The variation graphs of electrical conductivity and electrical resistivity with temperature and composition for Sn-[x] wt. % Zn [x=1, 9, 14, 50, 80] alloys are shown in Fig. 2 (a-b) and Fig. 3 (a-b).



(b)

Fig. 2. a) Electrical conductivity b) Electrical resistivity vs. temperature of Sn-x wt. % Zn (x= 1, 9, 14, 50, 80) alloys.



(a)



(b)

Fig. 3. a) Electrical conductivity b) Electrical resistivity vs. composition of Sn-x wt. % Zn (x= 1, 9, 14, 50, 80) alloys.

The dependence of electrical conductivity on temperature is often expressed as a slope in electrical conductivity vs. temperature graph and can be given as

$$\alpha_{ETC} = \left(\frac{1}{\sigma_0}\right) \left(\frac{\Delta\sigma}{\Delta T}\right) = \frac{\sigma - \sigma_0}{\sigma_0(T - T_0)} \tag{8}$$

where σ is the electrical conductivity of the solid phase at temperature T, σ_0 is the electrical conductivity at the initial temperature T_{0} and α_{ETC} is the electrical temperature coefficient. The electrical temperature coefficients for Sn-[x] wt. % Zn [x=1, 9, 14, 50, 80] alloys were obtained from the electrical conductivity vs. temperature graph and given in Table 1.

Sample	T ₀ (K	.)T (K)	κ ₀ (W/Km)	к (W/Km)	α _{TTC} (K ⁻¹)	σ (W-F) (Ω ⁻¹ m ⁻¹)	ρ (W-F) (Ωm)	α _{etc} (W-F) (K ⁻¹)
Sn-1 wt. % Zn	323	463	78.49	71.08	0.00067	0.0619	16.154	0.00262
Sn-9 wt. % Zn	323	463	86.39	75.42	0.00090	0.0659	15.163	0.00279
Sn-14 wt. % Zn	323	463	90.22	81.39	0.00069	0.0715	13.994	0.00263
Sn-50 wt. % Zn	323	463	101.123	87.06	0.00099	0.0783	12.763	0.00284
Sn-80 wt. % Zn	323	463	121.72	107.10	0.00085	0.1033	9.6837	0.00274

Table 1. Several thermal and electrical properties of Sn-x wt. % Zn (x = 1, 9, 14, 50, 80) alloys.

2.3. Determination of enthalpy change and specific heat capacity

The molecular structure and phase determine a material's specific heat capacity. Knowledge of the latent heat of phase transitions and the heat capacity of materials are required to understand phase transitions and the thermodynamics of materials. C_p = Specific heat capacity at constant pressure, and the heat supplied to the system will not increase its melting temperature. However, it will supply the enthalpy of fusion (the latent heat of melting) required to convert from solid to liquid. For a transformation from the solid phase to the liquid phase, enthalpy change can be expressed as

$$\Delta H = \Delta C_{p} \vec{n} \tag{9}$$

where T_m is the melting temperature and ΔC_p is the specific heat change.

The DSC (Perkin Elmer Diamond model) thermal analysis was performed in the temperature range of approximately 300-900 K with a heating rate of 1°C/min and under a constant stream of nitrogen at atmospheric pressure. The DSC curve of Sn-[x] wt. % Zn [x=1, 9, 14, 50, 80] alloys are shown in Fig. 4. The alloys' enthalpies of fusion (ΔH) were calculated as the area under the peak by integration. The values of specific heat change (ΔC_p) were determined by dividing it by the T_m temperatures of the enthalpies of fusion.



Fig. 4. Heat flow curves vs. the temperature for Sn-x wt. % Zn (x=1, 9, 14, 50, 80) alloys.

2.5. Structural Properties

The samples' surface morphology was investigated using a computer-controlled LEO 440 scanning electron microscope (SEM) equipped with an energy dispersive x-ray (EDX) spectrometer. The sample was cut transversely with ~ 2-4 mm thickness to obtain the SEM images. Transverse sections were ground flat with SiC papers and mechanically polished using 6 μ m, 3 μ m, 1 μ m, and 1/4 μ m diamond paste. Then, the etching process was also made to observe the microstructures on samples with 10 ml nitric acid and 90 ml distilled H₂O. The ratio of chemical compositions was measured by an EDX spectrometer attached to the SEM. SEM images and EDX analyses are shown in Fig. 5. A Bruker AXS D8 Advance Model XRD diffraction device was used to determine the grain sizes and crystal structure parameters of the samples; the powder diffraction patterns were taken at room temperature with a 40 mA current and a 0.02 °/s scanning speed (CuK_a radiation). Grain size (D) was obtained by using Scherrer's formula [37]:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{10}$$

where λ is the wavelength of X-ray used (1.5406 Å), β is the half-width of the peak with maximum intensities, θ is Bragg's angle. XRD diffraction patterns of samples are depicted in Fig. 6. The samples' crystal structural parameters vs. compositions and grain sizes (D_{sn} and D_{Zn}) are given in Tables 2 and 3, respectively.





Fig. 5. *SEM images and EDX analyses of Sn-x wt. % Zn (x= 1, 9, 14, 50, 80) alloys.*



Fig. 6. *XRD Patterns of Sn-x wt.* % *Zn* (x = 1, 9, 14, 50, 80) alloys.

Sample	a (Å)	b (Å)	c (Å)	V (Å) ³	20 (°)	d (Å)	Crystal System
	5.82823		3.17959	108.00	30.680	2.91179	Tetragonal
	5.83160*		3.18130*	108.19	32.060	2.78952	Tetragonal*
					43.920	2.05986	
					44.940	2.01543	
					55.380	1.65768	
					62.580	1.48314	
					63.840	1.45687	
					64.620	1.44116	
					72.477	1.30306	
Sn					/3.180	1.29226	
ure					/9.300	1.20389	
<u>.</u>	5.0215	5.0152	2.1710	107.20	89.461	2.011((Managhinia
	5.8215	5.8153	3.1/19	107.38	30.681	2.91100	Nonoclinic Data= 00.105
					32.090	2.78098	Beta- 90.195
					43.908	2.00038	
					44.000	2.03303	
					44.901	2.01455	
					55 300	1.65715	
					62 630	1.03713	
					64 671	1 44015	
Zn					72 468	1 30319	
t. %					73 310	1 29030	
1 w					79.580	1.20364	
Sn-					89.483	1.09432	
	2.66402		4.94651	30.40	36.297	2.47300	Hexagonal
					39.040	2.30532	5
					43.249	2.09022	
					54.349	1.68665	
					70.097	1.34135	
					70.697	1.33143	
					77.063	1.23655	
					82.073	1.17327	
					83.781	1.15364	
					86.569	1.12351	
					89.936	1.08998	
	5.82507		3.17762	107.82	30.710	2.90899	Tetragonal
					32.091	2.78692	
					43.969	2.05765	
					44.990	2.01333	
					55.431	1.65628	
					62.600	1.48272	
					63.860	1.45647	
Zn					64.670	1.44016	
%					72.500	1.30270	
wt.					73.222	1.29162	
6-u					79.580	1.20364	
Ś					89.511	1.09405	

Table 2. *XRD structural analyses of Sn-x wt. % Zn* (x = 1, 9, 14, 50, 80) alloys.

	2 65937	4 61228	4 94560	60.66	36 351	2 46944	Orthorhombic
	2.05757	1.01220	1.9 1500	00.00	20.052	2.10911	ormonionic
					12 200	2.30401	
					43.300 54.282	2.08/91	
					70.149	1.06571	
					70.146	1.34031	
					70.700	1.33139	
					76.941	1.23820	
					82.161	1.17224	
					83.844	1.15294	
					86.541	1.12380	
					89.930	1.09003	
_							
	5.8215	5.8090	3.1719	107.27	30.800	2.90070	Monoclinic
					32.180	2.77938	Beta= 90.039
					43.971	2.05759	
					45.050	2.01075	
					55.460	1.65548	
					62.660	1.48143	
					63.980	1.45402	
Zn					64.758	1.43843	
%.					72.590	1.30130	
wt					73.280	1.29074	
-14					79.654	1.20271	
Sn					89.556	1.09361	
	2.6610	4.6018	4.9389	60.48	36.380	2.46759	Monoclinic
					39.081	2.30305	Beta= 90.375
					43.338	2.08613	
					54.578	1.68012	
					70.249	1.33882	
					70.757	1.33045	
					77.148	1.23540	
					82.221	1.17153	
					86.695	1.12220	
					89.839	1.09090	
	5 83387		3 18294	108 33	30.638	2.91563	Tetragonal
	0100007		5110251	100.00	32.021	2 79282	8
					43 879	2.06168	
					44 898	2 01721	
					55 315	1 65947	
					62 513	1 48456	
					63 726	1 45920	
=					64 575	1.43720	
Z %					72 383	1 30451	
۲.					73 153	1 29267	
30 v					79.437	1 20545	
3-us					80 370	1.20545	
0 1	2 66520		4.04976	20.45	26 277	2 47427	Havaganal
	2.00550		7.740/0	30.45	38.079	2.30889	Tienagonal
					12 211	2.50888	
					45.211	1 69915	
					70.045	1.00015	
					70.045	1.34223	
					70.034	1.33246	
					17.023	1.23709	
					82.050	1.17354	
					86.543	1.12378	
					89.894	1.09038	

	5.83026	5.83360	3.18438	108.31	32.029	2.79218	Orthorhombic
					43.848	2.06307	
					44.840	2.01970	
					55.264	1.66088	
Zn					64.524	1.44308	
%					72.385	1.30449	
wt.					73.134	1.29296	
-50					79.474	1.20498	
Sn					89.383	1.09528	
	2.66992	4.61037	4.94934	60.92	36.255	2.47581	Orthorhombic
					38.951	2.31043	
					43.174	2.09371	
					54.386	1.68559	
					70.048	1.34218	
					70.683	1.33167	
					76.994	1.23748	
					82.071	1.17330	
					86.488	1.12435	
					89.901	1.09031	
	2.66314	4.94172		30.35	36.360	2.46888	Hexagonal
	2.66500*	4.94700*		30.43*	39.060	2.30424	Hexagonal*
					43.280	2.08881	
					54.401	1.68518	
					70.158	1.34033	
					70.700	1.33138	
					77.120	1.23577	
Zn					82.160	1.17225	
Ire					83.800	1.15343	
Ч					86.600	1.12318	

*Sn Literature: Proc. Phys. Soc., London, volume 67, page 737, (1954): Lee, J.A., Raynor, G.V. *Zn Literature: Natl. Bur. Stand. (U.S), Circ. 539, vol. 0, page 16, (1953) primary reference: Swanson, Tatge.

2.4. Investigation of Microhardness and Corrosion Properties

The mechanical properties, such as microhardness, mainly depend on the composition, microstructure, and processing temperature [38]. The mechanical properties of any solidified material are usually obtained by tensile strength test, hardness test, ductility test. Therefore, the mechanical properties were monitored by hardness testing since it is one of the easiest methods to apply to determine the structure's mechanical properties. The microhardness measurement was performed at room temperature using a hardness tester device (HMV-2 Micro Hardness Tester Shimadzu). The microhardness measured by the Vickers method is defined as the ratio of the load applied (in kg) to the projected area of the indentation (in mm²). Vickers hardness measurement was performed to clarify the relationship between microstructure and microhardness.

An optimum load value of 10 g was chosen, and it was applied for 10 s to the sample. Indentations were made at seven different places on the
sample to include hardness variation. The accuracy of the microhardness measurement was about $\pm 1\%$. Due to variation in crystallographic orientations of the sample, the average microhardness value was taken into account, and they are given in Table 3.

Samples	Vickers Microhardness	D, Grain Size (nm)	
	(Hv 0.01)	D _{sn}	D _{Zn}
Sn-1 wt. % Zn	11.50±0.11	125.66	45.20
Sn-9 wt. % Zn	12.60±0.12	114.60	53.60
Sn-14wt. % Zn	15.06±0.15	100.50	57.00
Sn-50 wt. % Zn	18.27±0.18	96.00	82.00
Sn-80 wt. % Zn	37.70±0.37	51.63	90.20

Table 3. Grain sizes and Vickers microhardness values of Sn-x wt. % Zn (x = 1, 9, 14, 50, 80) alloys.

The corrosion test was carried out by immersion method. The samples cut with the Secotom 50 precision cutting device were sanded in the range of 240-3000. Their polishing was completed using 9, 6, and 3 μ diamond suspensions. The initial weights of the polished samples were measured with a Kern brand precision balance. Then, their width, thickness, and height were measured using a caliper. A solution was prepared by adding 3.5% NaCl into pure water, and the samples were immersed in the solution and kept suspended for two days. Then they were removed at the end of the second day, dried, placed in a solution consisting of 18% chromic acid-pure water, and cleaned with ultrasonic polishing. They were kept here for 5 minutes, cleaned with alcohol, and dried, and their weight was measured again. The same procedures were applied for the other days. Weight loss vs. time and corrosion rate vs. time graphs are given in Fig. 7a and 7b.



Fig. 7. a) Weight loss vs. time graph, b) Corrosion vs. time graph of Sn-x wt. % Zn (x= 1, 9, 14, 50, 80) alloys.

3. Results and Discussions

3.1. The thermal conductivity and thermal temperature coefficient

The eutectic melting temperature of the Sn-Zn binary system is about 471 K. The thermal conductivities of the solid phase (kS) vs. temperature and composition of Sn-[x] wt. % Zn [x=1, 9, 14, 50, 80] alloys are shown in Fig. 1 and Table 1. According to the current experimental results, the thermal conductivity of Sn-Zn alloys linearly decreases with increasing temperature but linearly increases with increasing Zn's composition for a given temperature. The thermal conductivities vs. temperature of solid phases for pure Sn, pure Zn, and Sn-[x] wt. % Zn [x=1, 9, 14, 50, 80] alloys at approximately their melting temperature are obtained to be 60.60 \pm 4.84, 93.28 \pm 7.46, 71.08 \pm 8.52, 75.42 \pm 9.80, 76.08 \pm 6.08, 82.53 \pm 6.60, 89.62 ± 7.16 W/Km, respectively, and thermal temperature coefficients of the same materials are also calculated to be 0.00098, 0.00086, 0.00067, 0.00090, 0.00069, 0.00099, 0.00085 K⁻¹, respectively. In the current work, the obtained κ_s values are consistent with κ_s values of Sn-based alloys found by Arı et al. and Kaygısız et al. [39-41]. The thermal conductivity values differ depending on allovs' bulk stoichiometry and structural defects. In addition, phonon-phonon and phonon-electron inelastic scattering at high temperatures are more intense. Also, Sn-Zn solubility is limited due to the atomic radius, valence values, and crystal structures of Sn and Zn; crystal lattice is distorted, and while thermal conductivity with temperature is decreased, it is raised by increasing Zn composition.

3.2. The electrical conductivity, resistivity, and electrical temperature coefficient

The electrical conductivity and electrical resistivity vs. temperature and composition of Sn-Zn alloys are shown in Figs. 2-3. The variation of electrical conductivity and electrical temperature coefficients according to the component and temperature for the same materials were determined to be 0.0619 ± 0.007 , 0.0659 ± 0.007 , 0.0715 ± 0.008 , 0.0783 ± 0.009 , $0.1033 \pm$ $0.011 (1/\Omega m)$ and 0.00289, 0.00185, 0.00262, 0.00279, 0.00263, 0.00284,0.00274 K⁻¹, respectively, from the Wiedemann-Franz law by using the values of thermal conductivity, and are also given in Table 1. The dependency of electrical conductivity on the composition of Zn linearly increases with the increasing Zn composition for a given temperature. According to these results, the linear increase of the electrical conductivities for Sn-Zn alloys may be considered transmission provided by the maximum electrons on the composition of Zn. The number of mobile charge carriers in a metal depends on the carrier's concentration on Fermi energy. Free electron concentration in metals (finite temperatures like at room temperature) does not change with increasing temperature since it is already too high to contribute new electrons. The obtained κ_s values are consistent with Sn-based Sn-Zn and Sn-Cd alloys found with the four-point probe technique by Arı et al. [39, 40].

3.3. Determination of enthalpy change and the specific heat

Regarding DSC analysis of Sn-[x] wt. % Zn [x=1, 9, 14, 50, 80] alloys, the peaks are increased with increasing Zn composition. However, there are two peaks of Sn-50 wt. % Zn and Sn-80 wt. % Zn alloys. According to Sn- Zn phase diagram, Sn solubility in the Zn phase is negligible (less than 0.06 wt.%). Since the matrix phase creates Zn, two peaks, which belong to both Sn and Zn phases, occurred. The sum of the area under the two peaks for these alloys gives the fusion enthalpy. The specific heat capacities of Zn and Sn peaks are calculated by dividing the enthalpy of fusion changing by the melting temperatures that these peaks are observed. For other pure and alloy systems, specific heat capacity change is calculated by dividing the fusion enthalpy values, the area under the curve, by the melting temperature that peaks occurred. At melting temperatures, the enthalpy values of fusion (ΔH) of pure Sn, pure Zn, and Sn-[x] wt. % Zn [x=1, 9, 14, 50, 80] alloys were calculated to be 62.96 J/g, 113.19 J/g, 68.95 J/g, 71.71 J/g, 77.88 J/g, 95.64 J/g, 109.38 J/g, respectively. Also, the change of specific heat (ΔC_p) for pure Sn, pure Zn, and Sn-[x] wt. % Zn [x=1, 9, 14, 50, 80] alloys were detected to be 0.124 J/gK, 0.145 J/gK, 0.151 J/gK, 0.165 J/gK, 0.202 J/gK, 0.221 J/gK and 0.239 J/gK, respectively. In literature, the values determined for enthalpy of fusion for Zn and Sn are 108 and 58.9 J/g [42, 43], respectively, and the values of specific heat change for pure Zn and Sn are 0.390 0.117 J/gK [42-44], respectively. *△H* values for Sn-based alloys found by Wu et al. [45] have changed from 43.1 to 50.1 J/g, and ΔC_p values at 303 K from 0.210 to 0.269. There is no study involving the enthalpy and heat capacity changes according to composition and temperature for Sn-Zn alloys. However, our results seem to be in line with Wu et al.'s results, obtained from Sn-based alloys.

3.4. Structural Properties

The crystal structure and crystallization orientation were determined with XRD measurement (Fig.6). The crystal orientation, the diffraction angles and Bragg's interplanar spacing, crystal structures, and their parameters are given in Table 2. The average grain size (D) for Sn and Zn phases of each alloy system was calculated by the X-Powder computer program according to the higher intensity peak of XRD patterns using Debye Scherrer's Formula and are given in Table 3. In this study, the solubility decreases with increasing Zn, and the Sn phase gets thinner while Zn grain size increases. Similarly, as the amount of Zn increases, the tetragonal crystal structure will turn to a monoclinic crystal structure, then to orthorhombic, and finally to the hexagonal structure. Surface morphologies are explored by SEM with 20.000x magnification and given in Fig. 5. According to the SEM analyzes, the surfaces are made up of different-sized spheres. There is no crack on the surface. In the Sn-based Sn–Zn binary alloy, the acicular-shaped α -Zn phases are homogeneously distributed in the β -Sn matrix. While the matrix phase moves to Zn, in other words, Zn composition increases, grains tend to get a spherical shape, and a small amount of dissolved needle-like eutectic structure, which also contains the Zn phase, is located along the grain boundaries. The EDX profile and the elemental analysis confirmed that the phase consisted of Sn and Zn, as presented in Fig. 5.

3.5. Microhardness and Corrosion Properties

Microhardness measurements of Sn-[x] wt % Zn [x=1, 9, 14, 50, 80] alloys were calculated from average microhardness measurements of Sn and Zn phases and Sn-Zn grain boundaries in microstructures. Solidification conditions of Sn-[x] wt. % Zn [x=1, 9, 14, 50, 80] alloys are same. So, microhardness values only depend on the composition and the increase of Zn composition. Average microhardness values of Sn-[x] wt. % Zn [x=1, 9, 14, 50, 80] alloys are given Table 3. The variation of Zn amount highly impacts the grain size, and flake or needle shape distributions of Zn phase in Sn matrix result in different effects on hardness. Also, the microstructures shift from the tetragonal solid solution phase to the monoclinic and orthorhombic solution phase and then the hexagonal phase. Lattice distortion increases because of the difference in radii. Grain sizes increase by dissolving in each other with the increase of Zn composition. The grain boundaries between two different phases also form a barrier against the movement of dislocations, and dislocations in the grain boundaries with large-angle are accumulated in the grain boundaries and play an important role in increasing the microhardness of the alloy. In literature, the microhardness values of Sn-based Sn-1.2wt.% Cu [46] and Sn-9Zn-0.5Al [47] alloys are, on average, 11.36 and 18.3, respectively. The microhardness values of Sn-based Sn-Zn, Sn-Zn-Ag, Sn-8Zn-3Bi, Sn-8Zn-3Bi-0.25Ni, Sn-8Zn-3Bi-0.5Ni, Sn-8Zn-3Bi-1Ni alloys by Ahmed et al. [48] and Billah et al. [49] are in agreement with microhardness values measured in the current work.

As shown in Figure 7 in the 10-day immersion corrosion test results, the mass loss of Sn-[x] wt % Zn [x=1, 9, 14, 50, 80] alloys increases with the increase of Zn composition. The corrosion rate for all samples also increased with the increase of the Zn ratio in the structure. The sample with the highest corrosion rate is Sn-[14] wt. % Zn, the eutectic sample. The reason for the low corrosion rate in alloys with a high Sn ratio (Sn-[x] wt. % Zn [x=1, 9) is the formation of a passive SnCl₂ or SnO₂ thin film. The

formation of a ZnO thin film layer on the surface prevented the corrosion rate in alloys with a high Zn ratio (Sn-[80] wt. % Zn) [50].

4. Conclusions

The main conclusions of this review may be summarized as follows:

The thermal and electrical conductivity values for Sn-Zn alloys were investigated by using a radial heat flow apparatus. The thermal conductivity of the Sn-(x) wt.% Zn (1, 9, 14, 50, 80) alloys linearly decreases with increasing temperature but linearly increases with increasing Zn composition. The thermal temperature coefficients for Sn-Zn alloys were determined from the thermal conductivity vs. temperature graph. The electrical conductivity variation according to temperature for Sn-Zn binary alloys was also determined from the Wiedemann-Franz law by using the values of κ_s and L_{allov} . According to these results, the linear increase of the electrical conductivity for Sn-(x) wt.% Zn (1, 9, 14, 50, 80) alloys may have resulted from the transmission provided by the maximum electrons the composition of Zn. The number of mobile charge carriers in a metal depends on the carrier's concentration on Fermi energy. The electrical temperature coefficients were determined from the electrical conductivity vs. temperature graph. The enthalpy of fusion (ΔH) and the specific heat change values (ΔC_p) for Sn-x wt. % Zn (x=1, 9, 14, 50, 80) alloys were obtained by DSC, and good agreements are observed between our results and Wu et al.'s results, which are obtained for Sn-based alloys. The variation of Zn amount significantly impacts the grain size and flake or needle shape distributions of the Zn phase in the Sn matrix. The crystal structure of the alloys changed first from tetragonal to monoclinic, then hexagonal, and finally to the orthorhombic structure. In short, with the increase of Zn composition, some physical properties such as thermal conductivity of solid phases, electrical resistivity, change of fusion enthalpy, and change of heat capacity are increased. The increase of the Zn ratio in alloys increased the weight loss; the passive thin film layers formed on the surface of the alloys with high Zn and Sn ratios decreased the corrosion rates.

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