Modification of Natural Zeolite
for Anticorrosive Paint Preparation

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ABSTRACT: *Metal surface coating occupies an important place in the industry. The most important external factor on metal surfaces is corrosion. Corrosion is a natural process that occurs because of a chemical reaction between the metal surfaces and the medium. It causes the degradation of metals. Three methods are used the prevent corrosion. These methods are cathodic protection, anodic protection, and barrier coatings. In this study, it was aimed to develop environmentally friendly corrosion-resistant paint for the barrier coatings, by using zeolite material which has natural characteristics of corrosion resistance. In other words, it was aimed to gain the anticorrosive effect to the production of corrosion-resistant paint by adding modified natural zeolite to the paint. Microscale zeolite was modified by using lanthanum (III) nitrate, zinc acetate, and magnesium chloride solutions. The best results were obtained with a zeolite size of 0.8869 μm and using a 60% zeolite/solution volume ratio. It can be said from the results of the experiments that; thin zeolite film applications are very successful for corrosion resistance paint production. Modified natural zeolite coatings show a very good ability to protect surfaces from corrosion. The results of these procedures are positive and promising. The best result is obtained by zeolite with size reduction and 60% zeolite/solution by volume ratio. The amount of zinc phosphate was greatly reduced. High and low contents of zinc phosphates have almost the same anticorrosive effect with zeolite-modified paint formulations. As a result, cation-exchanged zeolites can be considered a safe and efficient alternative to traditional hazardous pigments in protecting steel surfaces.*

KEYWORDS: *Corrosion; Zeolite; Modification; Anticorrosive paint.*

INTRODUCTION

Paint has become important for industrial and household usage. Developments are made according to the problems to obtain more effective and quality products. One of the important problems is corrosion. Corrosion is the deterioration of metals because of a reaction between environment and metal surface. This is not a desired situation. Automobiles, planes, tanks, pipes, bridges, screws, and many important parts are made of metal and corrosion shortens the life of these. So, developments are made to give anticorrosive property for painting.

In traditional and old methods, chromium and lead-containing anticorrosive paints were used. Nowadays, these pigments are banned due to their bad effects on human health and the environment [1]. After the new formulation searching, investigators find the effect of zinc phosphate on corrosion. Corrosion could happen in acidic mediums and dissolved oxygen-containing mediums as known. It is not clear the prevention and inhibition mechanism of zinc phosphate and other corrosion inhibitors. Corrosion inhibitors are species that are added to a corrosive medium in a small amount to slow down and/or stop corrosion reactions on the metal surface. These inhibitors are adsorbed on the metal surface and form a protective thin film. In some cases, inhibitors could make chemical bonding with oxygen so corrosion could be prevented. So, there are some arguments and works to reach the mechanism of zinc phosphate. Firstly, when water permeates to paint film, part of zinc phosphate is started to hydrolyze and form phosphate and zinc ions. Phosphate and iron generate the stable iron phosphate that is inhibiting the anodic process of corrosion [2]. Also, this iron phosphate complex completes or maintains the film by filling gaps [3]. Second, zinc is also reacted with the hydroxyl of the water and formed insoluble hydroxides as zinc hydroxides that are deposited on the cathodic site of the steel surface, protecting it [4]. It is important to have enough amount of inhibitors in paint formulation to obtain a complete and successful corrosion inhibition effect on anodic and cathodic sites. The shielding effect is also one of the mechanisms of the anticorrosion effect of zinc phosphate on steel surfaces [5]. Zinc phosphate is a good alternative for chromium and/or lead-containing anticorrosive paint formulations but it is not a completely safe and eco-friendly selection. According to EC Regulations, zinc phosphate is reported as toxic to aquatic life and may be harmful if inhaled. An important point is that materials and methods for production should be as harmless as possible. For this reason, natural substances can be selected. Zeolites constitute a versatile material that has found many technological applications [6]. Zeolite is a material that is used in many technological areas it has a high ion exchange capacity. It is an alumina silicate mineral with a microporous structure that accommodates different cations, such as Mg^{2+}, Na^+, Ca^{2+}, K^+ and others. These different cations, such as Mg^{2+}, Na^+, Ca^{2+}, K^+ and others. These cations are rather loosely held and can readily be exchanged for others

in a contact solution [7]. Zeolite is a natural mineral that is found in nature and not classified as hazardous. Thanks to the sum of all these features, zeolites are used in energy, environment, construction, detergent, chemistry, medicine, mining, agriculture, and livestock sectors. All of this stability, porous properties, ion exchange capacity, and eco-friendly properties are made it also possible to use it in anti-corrosive paint formulations nowadays [8]. A simple mineral formula of zeolite is shown by $Na_2Al_2Si_3O_{10} \cdot 2H_2O$. It seems reasonable to change sodium cations in the zeolite structure with different cations that have corrosion inhibition potentials. The employment in paint technology is rather restricted, but zeolites have been used as humidity and ammonia adsorbent material in ceiling paints and finishing paints. Because zeolites are ionic-exchanging materials, it seemed reasonable to prepare anticorrosive pigment by exchanging sodium cations in zeolites with other cations that have inhibit properties [1].

There are different studies about the usage of zeolite after modification with different cations in anticorrosive paint formulations. Molybdic acid, lanthanum (III) nitrate, zinc acetate, magnesium chloride, and calcium carbonate-modified zeolites were used in anticorrosive pigment preparation [1, 9, 10]. There are some arguments and investigations about how zeolite provides an anticorrosive effect on coatings. These are mainly about the barrier mechanism and inhibition effects of zeolite. Insolubility and low water permeability of zeolite in water also strengthen the barrier effect [11]. *Pokmurshkii* and *coworkers* studied the inhibition effect of zeolite [12]. They used calcium-modified zeolite in paint film for inhibition mechanism in the subject to an acidic medium. *Toorani* and *coworkers* used lanthanum cations for corrosion inhibition in their study. Released cations make lanthanum hydroxide complex to form a protective layer for corrosion [13]. Solvent-based anticorrosive paints prepared by traditional methods emit toxic fumes and solvent vapors into the environment and their performance is insufficient for a long time. The anti-corrosive property of the coatings is provided by the use of resin-based and/or anticorrosive pigments. Especially with the use of epoxy resins, it is possible to give coatings highly anticorrosive properties. In addition, zinc compounds are generally preferred products in coatings due to their high anti-corrosive effect. However, because of the negative effects of these solvent-based systems on the environment and human health, the search

for new products continues. So the advantage of this study is to shed light on industrial production by researching suitable conditions and techniques for the production of corrosion-resistant paints prepared using natural type zeolite. And it was aimed to gain the anticorrosive effect on the production of corrosion-resistant paint by adding modified natural zeolite (clinoptilolite) to the paint. Because Clinoptilolite type natural zeolite is found in large quantities in many regions of our country. Turkey's natural zeolite mine production is reported as 60,000 metric tons/year in 2018 [14]. So, natural zeolites (clinoptilolite) obtained from Manisa/Gördes region were used in this study. Modification of clinoptilolite was obtained with lanthanum (III) nitrate, zinc acetate, and magnesium chloride at the laboratory conditions, and then paint that contains modified zeolite was tested on metal plates.

EXPERIMENTAL SECTION

In this study chemicals used in the modification of zeolite is zinc acetate dehydrate (Merck), magnesium chloride hexahydrate (Merck), calcium chloride (Merck), lanthanum nitrate hexahydrate; 99 %, and molybdic acid> 85% (Roth). Natural zeolites (Clinoptilolite) obtained from Manisa/Gördes region were in 0.8869 μ 60-70% zeolite/solution volume ratio used in this study. It is named 'hydrated sodium-potassium-calcium-alumino-silicate in general and is shown by the formula:

$(Na_{0.5}K_{2.5})(Ca_{1.0}Mg_{0.5})(Al_6Si_{30})O72.24H_2O.$
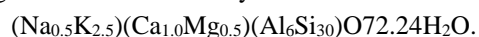
La (III) nitrate modification

Zeolite was placed in a beaker with 0.2mol/L HNO_3 (nitric acid). It heated up to the boiling temperature to eliminate ferric compounds. The zeolite was separated from the supernatant by filtration and washed with distilled water several times. Grade 1 filter paper which has 11 μm pore size was used. It was placed in a beaker 2 mole/L $NaCH_3COO$ (sodium acetate) for 3 hours under continuous stirring to put it back in the Na^+ form. The zeolite was separated by filtration and washed with distilled water. The zeolite was exchanged with lanthanum (III) ions by bringing it into contact with 1 mol/L $La(NO_3)_3$ (lanthanum(III) nitrate) in 1×10^{-3} mole/L HNO_3 under constant stirring for 24 h. The exchanged zeolite was separated by filtration, washed four times with distilled water, and dried at room temperature.

Zinc acetate and magnesium chloride modifications

Zeolite was impregnated in 75 ml of 0.1M Zn and Mg soluble salts. Stirring the solution for an hour was done at ambient temperature, and then the formed paste was filtered by using 11 μm pore size filter paper. These steps were repeated many times till it is assured that no more ion exchange can take place. Completion of the ion exchange process is determined and observed by the ammonium oxalate gravimetric method. In this method, ammonium oxalate solution (1 M) is adding the supernatant after filtration. The solution of ammonium oxalate will form a white precipitate of Zn and Mg oxalates if there are still free cations in the mixture. The ion-exchange zeolites were filtered, washed, and dried at room temperature. Characterization analyses were applied to the exchanged zeolites. These analyses were FT- IR, XRD, SEM, and SEM-EDS.

Addition of modified zeolite to paint formulation

Firstly, epoxy-polyamide-based primer paint with zinc phosphate content 10-15 vol% was prepared as a standard formulation. As the second step, modified zeolites were added to the zinc phosphate-free same epoxy primer paint formulation in approximately 10 vol%. The zeolite modification process was done with La, Zn, and Mg in this study. The dispersion of zeolite was made by the shaker process with the help of zirconium balls in 20-25 minutes. Particle size control was performed to test whether the shaker process was successfully applied. The fineness of the grinding value of the current paint sample should be maximum 25 microns. In these applications, the fineness of the grinding value of new paint samples was measured between 23-25 microns. Also, stability tests were performed to see the effect of modified zeolite added to the formulation of the paint. Paint samples with zeolites and standard formulations were stored at 40° C for 10 days to observe the change in their viscosity caused by precipitation, gelation, and solidification. A maximum increase of 10% in viscosity is acceptable. This viscosity term is basically defined as resistance to flow and it is expected to be within certain ranges. If viscosity is getting higher after adding some additive, for this study adding zeolite, affects application on surfaces and required solvent amount to thin the paint before. So, opacity could be decreased. Also, properties and technologies which are desired to give applied surface area decrease. For these reasons, an acceptable viscosity

increase is 10% to maintain the technology of paint. As a result of the stability test, it was found that there was no negative condition in the zeolite-containing samples and their viscosity was increased by 1-2% according to the initial viscosity values. After these steps, the paints were ready for application on steel plates and corrosion tests. Epoxy primer was applied to the steel test panels as a single layer in 100-micron dry film thickness. The curing condition was 80°C/50 minutes in the oven.

Characterization of modified zeolite samples

Modified zeolites with La, Zn, and Mg were characterized by FT-IR, XRD, SEM, and SEM-EDS analyses.

FT- IR spectroscopy of modified zeolite

The structural and chemical properties of zeolite after modification with different ions were performed in Perkin Elmer FT-IR (Spectrum 65) spectrophotometer with wave numbers between 4000 and 400 cm-1 in KBr pellets at room temperature.

X-Ray powder Diffraction (XRD) analysis of modified zeolite

XRD patterns were used to characterize the phase composition of the analyzed material, crystal structure, crystallinity, and defect of the materials with the help of characteristic peaks of materials [15]. It also gives a chance to observe a decrease or increase in crystallinity by comparing the intensity of peaks. XRD characterization of unmodified zeolite was carried out on the X-Ray Diffractometer (Philips XPert Pro) with XPERT-PRO diffractometer, X-ray tube anode: Cu and wavelength: 1.5406 A0 (Cu-K radiation), Ni filter properties.

Scanning Electron Microscopy (SEM) analysis of modified zeolite

SEM and SEM-EDS analyses of unmodified zeolite were done using FEI QUANTA 250 FEG. Other samples (modified zeolite) analyses were done using Carl Zeiss 300VP SEM-EDS device.

RESULTS AND DISCUSSION
Characterization of modified zeolite samples
FT-IR spectroscopy of modified zeolite

The most important and characteristic peak of the zeolite material should be seen at about 950-1200 cm^{-1} wavenumber (Fig. 1). For given FT-IR spectrums, these peaks are observed at about 1000 cm^{-1}. It means that the strongest Si/Al-O stretching vibrations appear at 1000 cm^{-1}. The exact position of bands depends on the Al/Si ratio of the material. It shifts to a lower wavenumber with the increasing number of Al atoms in the framework tetrahedral sites [16]. At the range between 3000-4000 cm^{-1} unmodified and modified forms of zeolites show broad and almost linear bands due to H-O-H bands of absorbed water. Some of these have small peaks at this range, it means water retention and absorption increased by modification with different chemicals [17, 18]. An FT- IR spectrum of clinoptilolite from literature is given in Fig. 1. Also, clinoptilolite which is obtained from the Gördes region is analyzed, and the FT- IR spectrum of this zeolite is given in Fig. 2 as unmodified zeolite. As seen from these figures, the characteristic peaks of both samples are shown in the same regions. It could be said that the zeolite used in the studies shows similar vibrations to the clinoptilolite in the literature.

FT- IR spectrums of LaZ, ZnZ, and MgZ are shown in Fig. 2. Characteristic peak of all three samples is shown in about 1000 cm^{-1} wave number and between 3000-4000 cm^{-1} broad and the almost linear band is observed due to absorbed water. This sample shows closer peak results to the unmodified zeolite sample as expected. Also, for LaZ sample, peak transmittances at the region between 1200-2000 cm^{-1} wave number are becoming a little more obvious. The main cause of the situation is probably strong La ions vibrations in this modification.

X-Ray Powder Diffraction (XRD) analysis of modified zeolite

XRD pattern of the Clinoptilolite from literature is given in Fig. 3. Clinoptilolite content of the given material is estimated at about 87-90% [20]. When compares with the unmodified zeolite pattern, there is some shift in peaks in 2θ direction and an increase/decrease in intensity. The reason for this situation is different Clinoptilolite content of zeolites. Characteristic peaks were observed at 2θ = 9.89°, 22.40° and 26.70° for XRD pattern of unmodified zeolite as shown in Fig. 4. According to data from 'The Structure Commission of the International Zeolite Association', two of these three peaks matched perfectly given the three characteristic peaks of Clinoptilolite [21]. The main peaks of unmodified zeolite belong to quartz, Clinoptilolite, and feldspar.
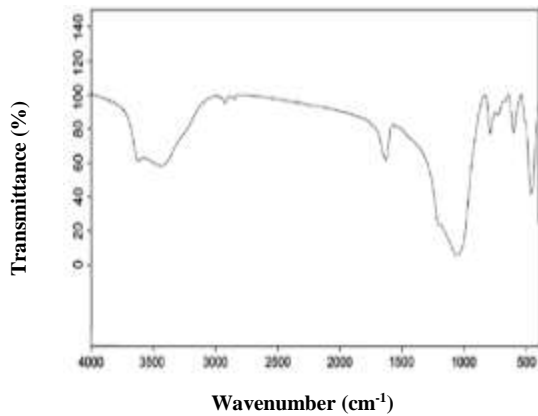
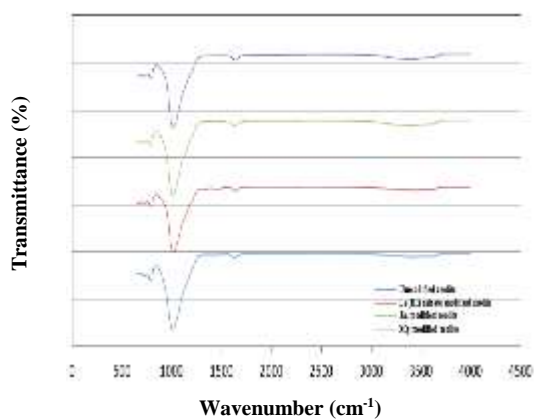**Fig. 1: FT- IR Spectra of Clinoptilolite [19].**

Fig. 3: XRD of Clinoptilolite [20].

Fig. 1: FT- IR spectra of Clinoptilolite [19].

Fig. 4: XRD of unmodified zeolite.

There was no collapse or destruction that appeared in different modified zeolites. All ion-exchanged zeolite samples possessed the almost same peaks as unmodified zeolite. It shows that the mineral structure of the zeolite is remained unchanged [22]. There was just some decrease and increase in peak intensities in the patterns. These obvious changes in patterns indicate that structural holes and the degree of crystallinity change [10]. Otherwise, an increase or decrease in the XRD peak intensities are not always an indicator of channel arrangement. The generation of XRD powder peaks results from the difference in the scattering power between the two building blocks in this case silicate wall and adsorbed ions [23]. By modification, the atomic scattering factor change in a given site, and this situation is probably the reason for increasing peak intensities. Additionally, distinctive sharpness and narrowed peaks are probably attributed to the increased cry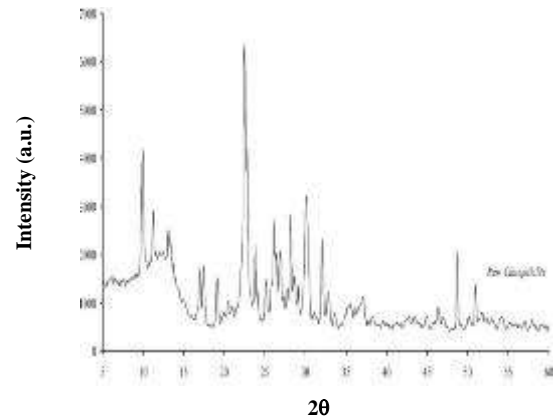stallinity of samples [24]. Results o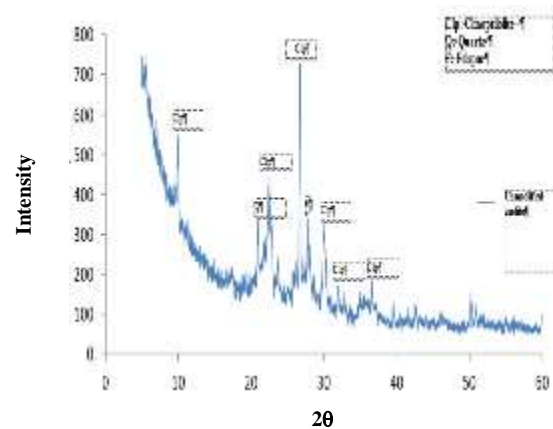f XRD analysis of LaZ, ZnZ, and MgZ samples are given in Fig. 5. Diffraction peaks of La, Zn, and Mg modified samples possessed almost the same structure except for differences in peak intensities. Also, a different peak is observed at about $2\theta=30°$ on LaZ pattern. This formation is confirming that La_2O_3 is loaded onto zeolite after modification [25].

Scanning Electron Microscopy (SEM) analysis of modified zeolite

The surface structure of unmodified zeolite was shown in Fig. 6 a. There was no pinned and different kind of zeolite mineral. Uniform, granular, and semi-platelet particles were observed. Platelet particles provide a positive effect in reducing water and gas permeability in paint formulas. It imparted a good anticorrosive effect [10].

Also, the highly porous structure of zeolite is clearly seen. This porous structure is made zeolite usable at ion-exchange procedures.

Table 1: Elemental compositions of unmodified and modified zeolite samples.

Element	Atomic % Unmodified Zeolite	Atomic % LaZ	Atomic % ZnZ	Atomic % MgZ
O K	62.54	46.48	47.14	43.40
NaK	0.58	2.29	2.51	-
AlK	5.44	7.39	10.77	1.65
SiK	26.22	35.46	33.87	27.89
K K	2.71	3.46	1.71	-
FeK	0.86	-	-	3.11
LaK	-	4.90	-	-
ZnK	-	-	0.66	-
MgK	0.45	-	-	15.08
CaK	1.21	-	3.36	8.86
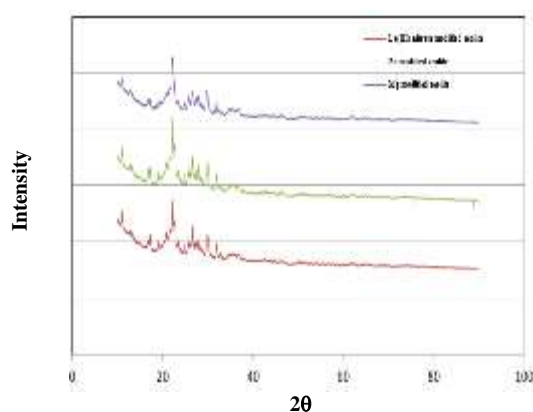
Fig. 5: XRD of La (III) nitrate-modified zeolite, Zn-modified zeolite, and Mg-modified zeolite.

With the help of SEM-EDS analysis, all of the elements in unmodified zeolite and modified zeolites are seen clearly (Table 1). As reported, used zeolite is containing a high ratio of silicon. With the help of these data, it is possible the make comment about the modification results of samples. It can also be evaluated whether the results are consistent with each other.

SEM micrograph and EDS results of modified zeolite samples are given in Fig. 6 b, c, d, and Table 1. Basically, particles show the same and partial platelet structure. The presence of doped ions on the surface of zeolite after the modification has been proved by EDS results.

The presence of exchanged ions is proof that modification is obtained successfully. These EDS results are supported by XRD analysis. XRD results of MgZ indicate that there is the formation of peaks of partially de-aluminated heulandite especially. As shown in Table 1, there is an evident decrease in at % of Al in MgZ sample. Si/Al ratio is one common characteristic of zeolites. There are significantly changing in Si/Al ratio in all modifications in this study. Si amount of natural zeolite is 26.22 %. When modifications were applied, this amount was increased to 35.46%, 33.87%, and 27.89% for La, Zn, and Mg, respectively. But Al amount of natural zeolite is 5.44%, when modifications were applied, this amount was increased to 7.39%, 10.87% for La and Zn, respectively. But this amount was decreased to 1.65% for Mg modification. The decrease and increase of Si/Al ratio indicated desilication and dealumination processes. This increase in the Si/Al ratio is caused by the dealumination process resulting from the removal of Al from the zeolite framework. These changes caused the formation of pores that are larger than the micropores of the natural zeolite [26, 27].

Fe is also not present in each three LaZ samples. It means that there is no ferric compound and elimination has occurred as desired due to procedure. For LaZ samples for each set, Ca is not detected. It is either completely exchanged or in a negligible amount. There is no exact correlation between the effect of zeolite size reduction and the used zeolite amount on the weight percent of elements in EDS analysis. Due to the change in the used solution for modification, the set which has more exchanged ion in weight percent is also change.
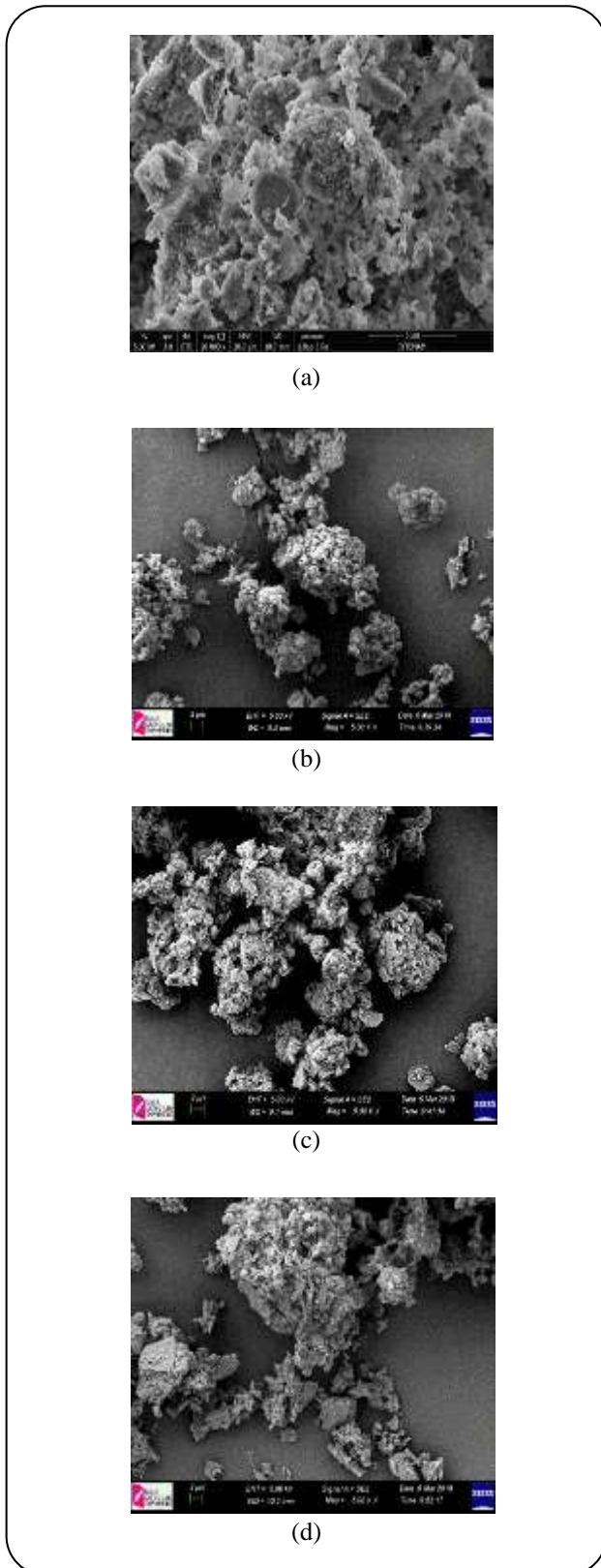
(a)

(b)

(c)

(d)

Fig. 6: SEM micrograph zeolite samples for a)unmodified b) LaZ c) ZnZ d) MgZ.

Corrosion tests

Corrosion tests were aimed to determine the corrosion resistances of materials by subjecting the materials to severely corrosive conditions. For the corrosion test, metal plates were scratched and painted by standard formulated anticorrosive paint which contains zinc phosphate in different amounts, and modified zeolite-containing paint in different film thicknesses. After curing, corrosion tests were started by placing the panels in a salt spray cabinet working as an ASTM B-117 standard. Curing was a process of transformation of organic film to a rigid film of thermosetting character because of polymerization reaction [28]. Evaluation of the results of corrosion tests was made by using ASTM D- 1654 (rusting in scribe) ASTM D-714 (blistering) and ASTM D-610 (rusting outside the scribe-surface rust) standards. ASTM B-117 is the most widely valid standard for the evaluation of salt spray testing. ASTM D 2247 is standard practice for testing the water resistance of coatings in 100 % relative humidity. ASTM D1654 was a standard corrosion test method that evaluates the resistance of painted or coated specimens after being subjected to different corrosive environments.

Corrosion tests were applied by using La, Zn, and Mg-modified zeolites containing paints at 500 h for the test period.

LaZ application: La modified zeolite containing epoxy-polyamide primer was applied as a single layer to steel test panels in 100 μ dry film thicknesses. Pictures of panels with detailed salt spray test results were shown in Fig. 7. LaZ sample provided the same blister size, density, and rust degree with low zinc phosphate-containing paint formulation. By this modification, a result as effective as the standard formulation was obtained.
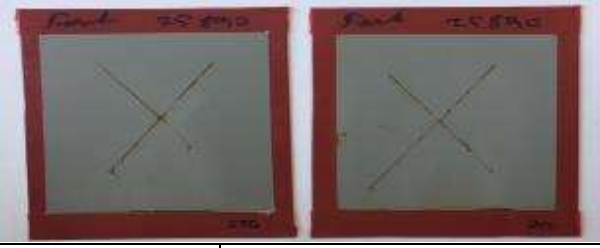
ZnZ application: Zn-modified zeolite containing the paint was applied to panels in 100μ film Dry Film Thicknesses (DFT). Pictures of panels with detailed salt spray test results were shown in Fig. 8. ZnZ sample provided the same blister size, density, and rust degree with low zinc phosphate-containing paint formulation successfully.

MgZ application: Mg-modified zeolite containing paint was applied to panels in 100 μfilm thicknesses. Pictures of panels with detailed salt spray test results were shown in Fig. 9. MgZ sample is showed same blister size, density and rust degree with low zinc phosphate containing paint formulation successfully.
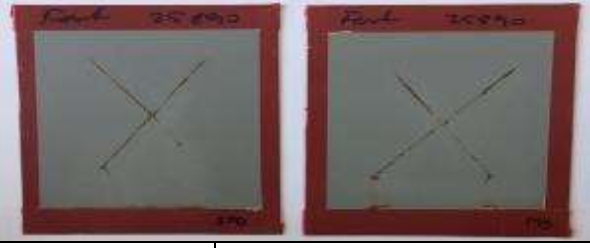
100μ DFT		
Anticorrosive Pigment	10-15% (Zinc Phosphate)	LaZ
Rust outside the scribe (ASTM D-610)	10-None	10-None
Blister (ASTM D-714)	None	None
Rust in scribe (ASTM D-1654)	9	9

Fig. 7. Application results for LaZ

Anticorrosive Pigment	10-15% (Zinc Phosphate)	ZnZ
Rust outside the scribe (ASTM D-610)	10-None	10-None
Blister (ASTM D-714)	None	None
Rust in scribe (ASTM D-1654)	9	9

Fig. 8: Application results for ZnZ.

Anticorrosive Pigment	10-15% (Zinc Phosphate)	MgZ
Rust outside the scribe (ASTM D-610)	10-None	10-None
Blister (ASTM D-714)	None	None
Rust in scribe (ASTM D-1654)	9	9

Fig. 9: Application results for MgZ.

Rust and blister test data are shown in Table 2. Modified zeolite-containing paint formulations provide excellent corrosion test results. All of the samples showed the same blister size, density, and rust degree as low zinc phosphate-containing paint formulation. Additionally, this study was carried out with thin film thickness paint application.

Table 2: Results of corrosion test.

	Zinc phosphate 10-15%	LaZ	ZnZ	MgZ
Rust outside the scribe (ASTM D-610)	10-None	10-None	10-None	10-None
Blister (ASTM D-714)	None	None	None	None
Rust in scribe (ASTM D-1654)	9	9	9	9

Table 3: Results of other performance tests.

Tests	ST Zinc Phosphate 10-15%	LaZ	ZnZ	MgZ
Adhesion	Gt- 0	Gt- 0	Gt- 0	Gt- 0
Gloss (60^0, gloss)	3	1.6	1.5	1.6
Hardness (persoz)	171	161	166	165
Elasticity (Conical Bending) (mm)	6	5	5	5
Impact Strength (Ib.in) (kg.m)	38 0.4378	38 0.4378	38 0.4378	38 0.4378
Stone Chip Resistance	7A	7A	7A	7A
Drying Time	80^0, 50 min	80^0, 50 min	80^0, 50 min	80^0, 50 min
Water Immersion (40^0, 7 days)	No color change No blister Gt-1	No color change Blister 4-medium, Gt-1	No color change No blister Gt-0	No color change No blister Gt-1
Humidity Resistance	No color change No blister No corrosion	No color change No blister No corrosion	No color change No blister No corrosion	No color change No blister No corrosion

Other Performance Tests Results

Zn, La, and Mg modified zeolite-containing epoxy-polyamide-based epoxy primer panels were applied to the following tests: Adhesion, Hardness, Impact strength, Elasticity, Stone chip resistance, Gloss, Water immersion, and Humidity; and evaluated according to the relevant standards by comparing with 10-15 % zinc phosphate-containing paint formulation (Table 3).

CONCLUSIONS

Zeolites are natural minerals noted for their ability toward ion exchange. So, exchangeable cations of zeolites could be changed by corrosion-inhibiting ions. These ions are made complexes and precipitate under the layer of metal surface as lanthanum hydroxide and calcium hydroxide. With the help of this property and the barrier mechanism of zeolite, it provides a good effect on corrosion prevention. La, Zn, and Mg cation-exchanged zeolites were prepared by using Clinoptilolite-type natural zeolite. This type of zeolite was obtained from Gördes/Manisa region. The advantage of this work is to use the natural resources of Turkey in industrial applications such as anticorrosive paint production. Because Clinoptilolite type natural zeolite is found in large quantities in many regions of our country. Turkey has the world's fifth-largest zeolite mineral reserves. And also, solvent-based anticorrosive paints prepared by traditional methods emit toxic fumes and solvent vapors into the environment and their performance is insufficient for a long time. Anticorrosive paint formulas with zeolite modification are new methods and less harmful to the environment. This study is also valuable because it is carried out by using the resources of our country.

The results of these procedures are positive and promising. The most effective results were obtained with a volume ratio of 60% zeolite/solution and 0.8869 μm zeolite sizes. If the results are compared for modified and unmodified zeolites, it can be easily seen the differences from each characterization method. If the peaks that are given at modification of La, Zn, and Mg in Fig. 2 compared with unmodified zeolite peak, are seen with different peaks obtained in these analyses. The other evaluation of the modifications of La, Zn, and Mg cations to the natural zeolite can be explained with XRD analysis. If Fig. 4 is compared with the Fig. 5, modifications of La, Zn, and Mg are seen with diffraction peaks obtained in these analyses. SEM-EDS analysis also shows the modifications of La, Zn, and Mg cations to the natural zeolite.

Anticorrosive paint formulas with zeolite modification are the new method and less harmful to the environment. In addition, Turkey has the world's fifth-largest zeolite mineral reserves. This study is also valuable because it is carried out by using the resources of our country.

The amount of zinc phosphate was greatly reduced. High and low content of zinc phosphates have almost the same anticorrosive effect with zeolite-modified paint formulations. So, it can be concluded that cation-exchanged zeolites can be considered a safe and efficient alternative to traditional hazardous pigments in protecting steel surfaces.

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