Investigation on metal coating's endurance through corrosion

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Abstract

In daily life, metals are used in everywhere and they are the main parts of technical and mechanical devices. They should be strength enough to endure the conditions in the environment such as pressure, forces, temperature and the hardest one corrosion. Metals have some processes to increase their endurance through such difficulties. One of the easiest ways to increase the metal's endurance is coating. This method is used in almost all areas such as engineering, ships and electrical devices and even in mechanic industry for protection and endurance.

One of the most important areas of metal coating is to inhibit corrosion in metal surface. Metals react with oxygen in daily life. To prevent these oxidation reactions metal coating is used. Zinc, chrome, platinium, etc. Are commonly used in coating metals due to their low oxidation potential they have.

In this study, the research was chosen to be "Would endurance for corrosion of different coated metals in salt solution be different?" Zinc, chrome, iron, copper and nickel coated metals, made by same factory and by the same process, was used in the study. Salt solutions prepared and coated metals were sink into these solutions to observe the corrosion or changes.

Some changes such as colour change on the metal surfaces and salt solutions were observed at the end of the experiment. All changes were noted in 5 day interval and after a 30 day period, the metals were compared with each other respect to these changes. It is realised that the best metal which has best endurance to corrosion is chrome. Because, after the 30 day period there is no evidence which shows chrome corrodes. The endurance of metals to corrosion goes from most endurance to less one as copper, nickel, iron, zinc.

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Introduction

We use chemistry in all areas of our lives. Chemistry's one of the most useful areas in daily life is development on metals and their properties. We came across with metals in our daily life but we even did not know how they produce or how they protect us. However it is certain that the process called coating we use, makes these metals stronger and increase their endurance for corrosion. So, why we need to use metal coatings on metals? Are metals not strong enough to not corrode?

Corrosion: Metals corrode because we use them in environments where they are chemically unstable. Only some of metals such as gold, silver and platinum are found in nature in their metallic state. All other metals except these are produce after some process. Therefore, almost all metals are unstable in their area of usage.¹

We came across with lots of metal building or statue around the world. However most of these sculptures and statues are made of metals, which make these statues defenceless and stalky. The reason why they are defenceless in their area of usage is that these metals have tendency to be more stable. Tendency to be more stable can be expressed as corrosion and this is why some protective films used to slow down corrosion process. We can also avert corrosion process by using metals, form natural protective films. Corrosion has many serious economic, health, safety, technological, and cultural consequences to our society.

Economic effects

Studies in a number of countries were carried out to determine the cost of corrosion. The study which is carried out in the United States in 1976 showed that the overall annual cost of metallic corrosion to the U.S. economy was \$70 billion, or 4.2% of the gross national product.²

Health effects

Metals another area of usage is medical in prosthetic devices in the body, such as pins, plates, hip joints, pacemakers, and other implants. Again corrosion obstructs these metals proper use by broken connections in pacemakers, inflammation caused by corrosion products in the tissue around implants.

¹ Retrieved November 29, 2010, from Corrosion Technology Laboratory Web Site: http://corrosion.ksc.nasa.gov/corr_metal.htm

² Retrieved December 5, 2010, from Electrochemistry Encyclopedia Web site:

http://electrochem.cwru.edu/encycl/art_c02-corrosion.htm

Safety effects

Another problem of corrosion came across in structures. Corrosion decrease the life time of metal structures and mechanics as corrosion weakens metals and metals cannot use as they are designed for.

> Technological effects

As it is mentioned above there are economic results of corrosion and technology directly affected by these results. New studies are made to solve corrosion problem to able metal use in high temperatures, high pressures and convenient conditions for corrosion. Geothermal systems, which has suitable conditions for corrosion and solar energy systems are some examples of struggle conditions for metals to be used while preventing them from corrosion.

Cultural effects

In world, lots of cultural statues were made with metals; this is a problem when metals can corrode with the process of corrosion. For that reason governments find new solution to prevent their cultural artifacts destroy by corrosion.

In this essay the general (uniform) corrosion will be investigated.

General (Uniform) Corrosion

The surface effect produced by most direct chemical attacks (e.g., as by an acid) is a uniform corrosion of the metal. On a polished surface, this type of corrosion is first seen as a general dulling of the surface and, if allowed to continue, the surface becomes rough and possibly frosted in appearance. The discoloration or general dulling of metal created by its exposure to elevated temperatures is not to be considered as uniform corrosion. The use of chemical-resistant protective coatings or more resistant materials will control this problem.³

To investigate the process of coating and the endurance metals will show, basics of electrochemistry and the terms of it should be known.

Electrochemical Cells

Oxidation and Reduction: Metals are elements that tend to lose electrons when they are involved in chemical reactions, and non-metals are those elements that tend to gain electrons.

³ Retrieved November 28, 2010, from Corrosion Technology Laboratory Web site: http://corrosion.ksc.nasa.gov/unifcor.htm

Sometimes these elements form ions, charged elements or groups of elements. Metallic ions, because they are formed from atoms that have lost electrons, are positively charged (the nucleus is unchanged). When or ion loses electrons it is said to have been oxidized. an atom A common oxidation reaction in corrosion is the oxidation of neutral iron atoms to positively charged iron ions:

 $Fe \rightarrow Fe^{+2} + 2e^{-2}$

The electrons lost from a metal must go somewhere, and they usually end up on a non-metallic atom forming a negatively charged non-metallic ion. Because the charge of these ions has become smaller (more negative charges) the ion or atom which has gained the electron(s) is said to have been reduced.

 $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$

 $2H^+ + 2e^- \rightarrow H_2$

While other reduction reactions are possible, the reduction of oxygen is involved in well over 90% of all corrosion reactions. Thus the amount of oxygen present in an environment, and its ability to absorb electrons, is an important factor in determining the amount of oxidation, or corrosion, of metal that occurs.⁴

In this experiment the corrosion can be defined as wet corrosion. In wet corrosion the system comprise from a metal and an aqueous solution. A corrosion process can arise from anodic and cathodic reactions. In this experiment the oxidation of metals is anodic reaction and at the end of this process metal dissolve to its cations. Such as Cu metal oxidates and Cu^{+2} ions are obtain. On the other hand oxygen, which aqueous solution contains, reduced. All this electrochemical reactions happened without using an external electrical circuit or charge.

However, this process needs a solution which can conduct electricity. The reason for this is that to maintain a cathodic reaction the electrons which was released by metal oxidation should be in the cathodic reaction zone. Electrolyte or table salt solution able to conduct electrons to cathodic reaction zone which enable to maintain an electrochemical reaction, corrosion. Using salt solution is an important factor in increasing the rate of corrosion since salts produce cations and anions in solutions; this is why they are called electrolytes. Electrolyte allows a current of electricity to pass through the solution which includes a salt, also the negative and positive particles of salt. By that all necessary conditions for an electrolytic reaction is ready to be which causes metals to be oxidized and become metal cations. The metal cations dissolve in the salt solution and contribute an increase in the electrical current in solution. NaCl dissolves into Na⁺ and Cl⁻ ions if water is present. These anions conduct

⁴ Retrieved December 2, 2010, from Corrosion Technology Laboratory Web site: http://corrosion.ksc.nasa.gov/electrochem_cells.htm

electricity and this makes salt solution more conductive. By this method the rate of corrosion increases. Cl^{-} ion is a strong reducing agent. Therefore, it attacks the iron (III) oxide layer and disclosures a new layer which also speeds up the rate of corrosion. These properties of salt make it a good provider for corrosion.

Wet corrosion reactions are only possible if the free energy of the products of reaction is lower than that of the reactants. This is the case however for the reaction of nearly all metals with water and oxygen to give metal hydroxides:⁵

$M{+}H_2O(l) \rightarrow M(OH)_2(s)$

Furthermore, the rate of wet corrosion may often be very high compared with dry corrosion on the same metal at the same temperature. There are two underlying reasons for this:

The dipolar water molecule stabilizes the free (dissociated) metal ions in solution and the metallic structure and water in contact with it can both conduct electric current. This enables the corrosion reaction proceed through the coupling of two primary corrosion reactions:

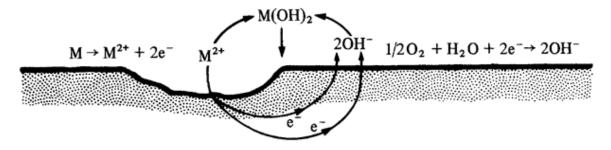
 $A: M \rightarrow M^{2+} + 2e^{-}$

(Anode reaction: destroys metal, releases electrons, oxidation)

$$C: 2e^{-} + H_2O + 1/2 O_2 \rightarrow 2OH$$

(Cathode reaction: consumes electrons; electron sink reaction: reduction).

Electrons liberated in the anode reaction A flow to the site of the cathode reaction C through the conducting metal. The movement of dissociated ions carries an equal ionic current in the water. The distances over which these currents flow can vary from microns to many metres. All wet corrosion processes can be analysed in terms of anodic and cathodic reactions. The anodic process is the direct cause of damage to metallic structures but both an anodic and a cathodic process must occur for a corrosion cell to be formed.⁵



Picture 1: Wet corrosion of M metal

⁵ Retrieved December 17, 2010, Web site: http://cmse.ed.ac.uk/mse3/topics/mse3-corrosion.pdf

Cathodic Protection:

Cathodic protection has become a widely used method for controlling the corrosion deterioration of metallic structures in contact with most forms of electrolytically conducting environments, i.e. environments containing enough ions to conduct electricity such as soils, seawater and basically all natural waters. Cathodic protection basically reduces the corrosion rate of a metallic structure by reducing its corrosion potential, bringing the metal closer to an immune state. From a thermodynamics point of view, the application of a CP current basically reduces the corrosion rate of a metallic structure by reducing its corrosion potential towards immune state.⁶ its

After learning some terms about electrochemistry and its terms it will be easy to understand the process of coating. To start with, the steps of coating process and the bond characteristics of each metal used in this experiment should be known to investigate their strength in using them as coating metal.

The metals used in this experiment have same process to be coated with zinc, iron, chrome, copper and nickel. The strength of the metals is different because each metal has its own oxidation and reduction value. The force makes the coated or non-coated metals to the corrosion or any other chemical change in their environment is the strength of their ionic bonds.

To shorten the process of coating; the metal, which was negatively charged by an energy source, put into the solution where solution includes positively charged ions of the metal which wanted to be coated. As it is the basic rule negative charged particle attract the positive ions in the solution metal put into the solution oxidized by positive particles. This is known as coating process although it has some detailed process.

Other Factors in Rate of Corrosion

Firstly, the more active the metal, the more corrosion occurs. In daily life we can use less active metals such as gold and stainless steel but they are too expensive and heavy for use so coating is the best way to protect metals from corrosion.

Secondly, an electric current, an energy source can be used in this experiment to fasten the reaction more. This change will decrease the period of oxidation process. However, in this experiment no energy source was used to fasten the reactions. Instead of this, the period of observation enlarged.

⁶ Retrieved November 29, 2010, from Corrosion Doctors Web site: http://corrosiondoctors.org/CP/Introduction.htm

In this experiment five different coated metals, one is uncoated, will be compared to determine which metal coating procedure is the most beneficial is and why.

Aim: To compare the endurance of metals which are coated with different metals (nickel, iron, copper, chrome and zinc) To find out which coating way is the most useful?

Research Question: Would the endurance for corrosion of different coated metals in salt solution be different under the same conditions?

Dependent Variables: Different resistance the coated metals show in salt solution.

Independent Variables: 5 different coated metals which is totally 15 metals will be coated

Controlled Variables:

- Aluminum rods: Coating was done on aluminium rods.
- Same coated metals have same coating process.
- The temperature of the experiment room is constant with 25 °C.
- The time period metals will be in salt solution is 30 day.
- Molarity of each salt solution is same because salt solutions are prepared with same amount of salt and same volume of water.
- Concentration of each table salt solution is same.
- Surface area of coated metals is same. Total surface area of each metal is 70.65 cm².
- Pressure of the room is same as the experiment took place in same room for 30 day period.
- Size of corrosion cell: Production of same manufacturer used $150ml \pm 2ml$.

Materials:

- 3 iron coated metals
- 3 copper coated metals
- 3 nickel coated metals
- 3 chrome coated metals
- 3 zinc coated metals
- 150ml Beaker $(x15) \pm 2$ ml
- 1,5 kg table salt
- 3L water

Procedure:

- 1. Put 72 grams of table salt into each beaker.
- 2. Add 200 mL of water to each beaker to make a salt solution.
- 3. Stir the salt solution until all salt in the bottom of the beaker solved.
- 4. Clean all metals not to cause any errors in experiment.
- 5. Label each beaker with the name of the metal it will contain such as iron, zinc, chrome and nickel.
- 6. Put all coated metals into the salt solution.
- 7. Observe each metal in 5 day arrivals with in a period of 30 days.
- 8. Take all metals from salt solution after 30 day period.
- 9. Compare each coated metal groups by the changes in their appearance.

Data Collection:

Day 5: (see Picture 3 in Appendices to see all metals in the salt solution)

Nickel: There is no change in solution's colour and in the metal.

Copper: Solution's colour change to a yellowish colour.

Iron: There are little black points in the metal surface, also solution is yellowish.

Zinc: Solution's colour change to a yellowish colour.

Chrome: No change observed.

Day 10: (see Picture 4 in Appendices to see all metals in the salt solution)

Nickel: Colour of solution become yellowish.

Zinc: There are black points in the metal surface but solution's colour is still yellowish.

Chrome: No change observed.

Iron: Black points grow and spread over the metal. Solution's colour is between yellow and orange.

Copper: Solution's colour still yellowish and the metal is less gloss.

Day 15: (see Picture 5 in Appendices to see all metals in the salt solution)

Nickel: Colour of solution is yellow, some solid particles seen in the bottom of the solution.

Zinc: Black points grow but still there is no change in solution's colour.

Chrome: No change observed.

Iron: Solution's colour seems like orange and black points are so much that metals surface is black now. Tiny metal particles sink to the bottom of solution.

Copper: Colour of solution is yellow.

Day 20:

Nickel: Colour of solution is yellow. Still there is no change in metal's surface.

Zinc: Black points are still growing however there is no change in solution's colour. Tiny metal particles sink to the bottom of solution.

Chrome: Solution becomes yellowish but there is no change in metal's surface.

Iron: Still same as 15th day.

Copper: Metal loses its glossiness. Solution's colour is dark orange. Tiny metal particles sink to the bottom of solution.

Day 25: (see Picture 6 in Appendices to see all metals in the salt solution)

Nickel: Solution's colour is dark- orange, metal loses its glossiness and colour change to light orange.

Zinc: There black points spread over. No change in solution's colour.

Chrome: Solution has a yellowish colour but no change observed in metal.

Iron: Iron completely became black-rusted. Solution's colour is terracotta.

Copper: Metal's orange colour change into light orange while solution's orange colour became darker.

See Picture 7 in Appendices to see all metals after the experiment

See Picture 8, 9, 10, 11, 12 and 13 in Appendices to see the changes in each metal after the experiment.

Data Processing:

As it is mentioned in the introduction part, metals have tendency to lose electrons which is called as oxidation.

In the beginning of the experiment, all solutions include Na^+ , Cl^- coming from NaCl, H^+ , OH^- ions coming from self-ionization of water, dissolved O_2 molecules and the water molecules.

The anodic and the cathodic reactions that occur on a metal surface in corrosion cells as follows.

In the salt solution containing Nickel; Metal will react with O_2 molecules as O_2 is a good reducing agent, to lose electrons and become oxidized. O_2 and metal bind each other to form a new compound and weakening the bonds of the metal itself. This is why surface of the metals affected in this experiment. The net reactions can be written as;

Cathodic Reaction:
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH$$

This is the cathodic reaction occurs in corrosion in natural environments where corrosion occurs at nearly neutral pH values.

Corrosion Cell Reaction: $2Ni + O_2 + 2H_2O \rightarrow 2Ni(OH)_2$

In the case of zinc, the net reactions can be written as;

- Cathodic Reaction: $O_2 + 2H_2O + 4e^2 \rightarrow 4OH^2$
- Anodic Reaction: $Zn \rightarrow Zn^{2+} + 2e^{-1}$

Corrosion Cell Reaction: $2Zn + O_2 + 2H_2O \rightarrow 2Zn(OH)_2$

In the case of Chrome, the net reactions can be written as;

- Cathodic Reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
- Anodic Reaction: $Cr \rightarrow Cr^{+3} + 3e^{-1}$

Corrosion Cell Reaction: $4Cr + 3O_2 + 6H_2O \rightarrow 4Cr(OH)_3$

It seems reasonable that Chrome gives three of its electrons in oxidation reaction and the total reaction is taken by summing the anodic and cathodic reactions. However, a rust or oxide compound should be obtained to see corrosion in the metal surface. This reaction is special for chromium(III)(Cr^{+3}) like;

$$2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{-2} + 14H^+ + 6e^- E^0 = (-)1,33 V$$

The electrode oxidation potential of chrome is a negative value which means that this reaction cannot take place spontaneously. Therefore, corrosion or rust formation reactions of chrome decrease the potential difference of overall reaction. This reaction's potential difference will added to the overall reaction.

In the case of iron; the net reactions are as follows;

Cathodic Reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Anodic Reaction: Fe \rightarrow Fe²⁺ + 2e⁻

Corrosion Cell Reaction: $2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$

Though there is an extraordinary situation for the Iron, called as rust formation. Net product of oxidation of Iron is known as Fe^{2+} and H_2O , but Fe^{2+} reacts with the O_2 which is present in the air. At the end of these reactions Fe_2O_3 is produced which is known as rust. These reactions can be written as;

$$4 \operatorname{Fe}^{2+} + \operatorname{O}_2 + 6\operatorname{H}_2\operatorname{O} \rightarrow 2 \operatorname{Fe}_2\operatorname{O}_3 \cdot \operatorname{H}_2\operatorname{O} + 8 \operatorname{H}^+$$

In the case of copper, the net reactions are;

Cathodic Reaction:	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Anodic Reaction:	$Cu \rightarrow Cu^{2+} + 2e^{-}$
Corrosion Cell Reaction:	$2Cu + O_2 + 2H_2O \rightarrow 2Cu(OH)_2$

As all the reactions are shown above, it can be said that all reactions look same as all coated metals lose two electrons to reduce O_2 to form metal hydroxides. However, the tendency of metal atoms to give electrons is different from each other. The difference in the values could be explained by the potential difference occurred in these reactions, which is known as standard electrode potential of metals and denoted by E^{θ} .

The standard potential of the corrosion cell can be calculated by summing the reduction (cathodic) and oxidation (anodic) potential in the cell.

Cathodic Reaction:	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	$E^{e} = 0.40 V$
Anodic Reaction:	$Ni \rightarrow Ni^{2+} + 2e^{-}$	$E^{\theta} = 0.23 V$
Corrosion Cell Reaction:	$2Ni + O_2 + 2H_2O \rightarrow 2Ni(OH)_2$	$E^{e} = 0.63 V$

To obtain the corrosion cell potential for net reactions same calculations were done.

This process was done in each case and corrosion cell potential ($E^{e}_{corrosion}$) were calculated. These values are given in the table below;

Electrochemical cell	Standard Potential
Zinc corrosion cell	$E^{0} = 1.16 V$
Iron corrosion cell	$E^{e} = 0.84 V$
Nickel corrosion cell	$E^{0} = 0.63 V$
Copper corrosion cell	$E^{e} = 0.06 V$
Chrome corrosion cell	$E^{e} = -0.36 V$

Table 1: Standard potential of corrosion cells.

Reduction and Oxidation potential values are taken from IBID Chemistry book⁷

By this information, the endurance of the metals to the corrosion should be like that, chrome has the most significant endurance to the corrosion. This sequence goes from most to less like with copper, nickel, iron and zinc. The reason for this is that each corrosion reaction has different cell potential which shows the tendency of the reaction to take place. Therefore we can conclude that greater cell potential greater tendency of the reaction to occur.

⁷ Green J & Damji S. (2008) IBID Chemistry, 3rd Edition: IBID Press

Conclusion:

In this experiment significant and common changes were observed and used to compare metal coatings endurance. These significant and common changes are; colour-change in salt solution, metals glossiness, rust formation at the bottom of the beaker and black rust points observed on metal's surface.

In this experiment first significant changes observed in Iron and Zinc metal with black points, which observed on the surface of the metals, called rust. In addition, in Zinc, Iron and Nickel corrosion cell salt solution's colour changes into yellowish colour. In the beginning, the colour of the solutions was milky, due to the dissolved table salt. However, after a period of time the colour of coppers cell turns into dark orange.

The reason for this is that the cations formed by metal gave their colour to the solution. Moreover, on the 10th day some black points were observed on the metal's surface. These black points can be the weakest part of the coating. As coated metal leave the base metal, base metal came into the contact with salt solution. This was a good reason to tell that they are not resilient to the corrosion. On the other hand, there are no significant changes observed in Chrome and Copper for first 15 days, but then Copper metal started to lose its glossiness. Actually it is just a fact that coating metal loses its electrons and did not bind with the base-metal anymore and make surface of base metal rough and rugged which causes metals to lose its glossiness.

However, Chrome metal had no significant changes in the whole 30 day period. The reason for these changes can be explained by corrosion cell's potential difference.

In Data Processing, standard potential of each corrosion cells were given. These values can be taken as expected values because the standard potentials of each corrosion cell determines if the corrosion will take place or not. For reaction to take place in a corrosion cell, there must be a potential difference between two half cells. According to the expected values given in the Table1 the first changes should be observed on Zinc and Iron which was just like what happening in the experiment. Nickel and Copper comes after them, which was just as in the experiment. However, chrome did not corrode because of its negative standard potential which means that salt solution and water is not enough for chrome to corrode but also a charge, an electric circuit needed.

How to reduce error?

✓ Observations are the main source of data in this experiment. However, data collected in this experiment can be specified if quantitative data collected. For example, the thickness of metals or the weight of metals can calculate to find out a relation with metal's endurance to corrosion and the weight loss of the metal(or even rate of corrosion).

- ✓ The difference between each metal's endurance toward the corrosion is about that metal's standard potentials. In this experiment no energy source had been used because most of the reactions happened spontaneously. However, if an electric source was used changes would be observed significantly in a shorter time period. So the experiment can be set with an electric source which speeds up the reactions and also reduces the error in experiment.
- ✓ 3 samples used for each type of coating metal. However, to reduce error, 5 or more samples can be used to observe changes, to get common results. By this way more stable results will be taken and error percentage will decrease.

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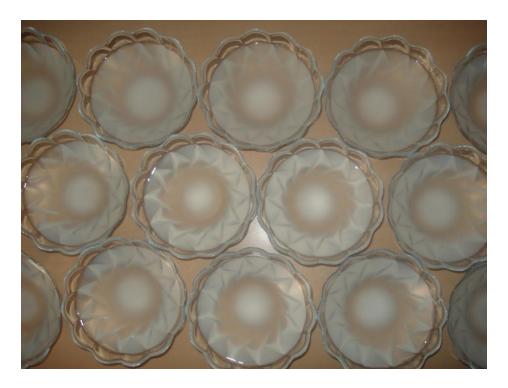
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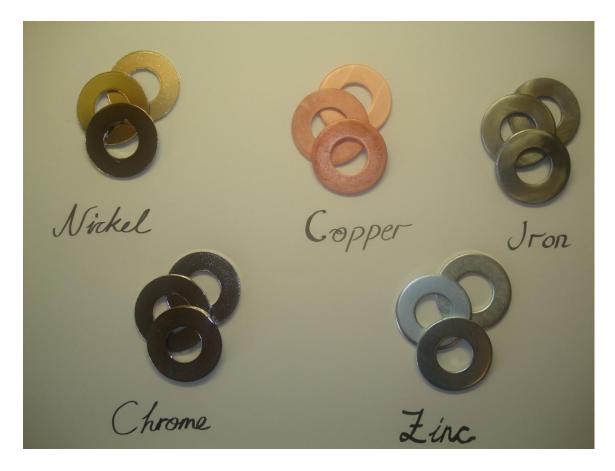
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⁷ Green J & Damji S. (2008) IBID Chemistry, 3rd Edition: IBID Press

APPENDICES



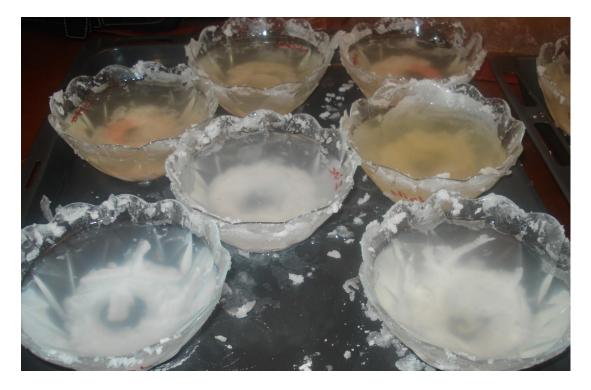
Picture 1: Preparation of salt solution



Picture 2: View of all different coated metals in the beginning of the experiment.



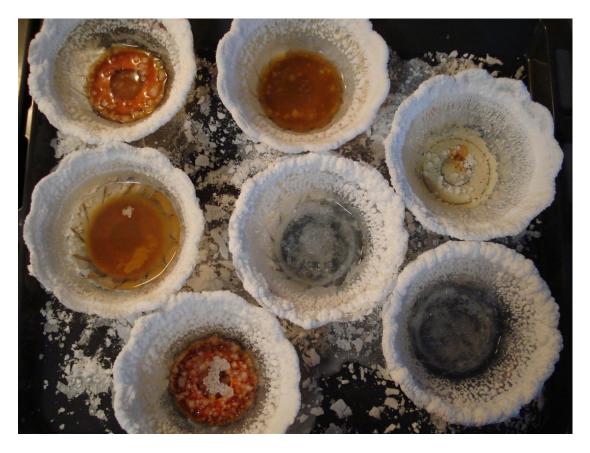
Picture 3: 5th day of experiment



Picture 4: 10th day of the experiment



Picture 5: 15th of the experiment



Picture 6: 25th day of the experiment



Picture 7: View of all different coated metals at the end of the experiment.



Picture 8: Pictures of chrome metals before experiment and after experiment



Picture 9: Pictures of zinc metals before experiment and after experiment



Picture 10: Pictures of 1ron metals before experiment and after experiment



Picture 11: Pictures of copper metals before experiment and after experiment



Picture 12: Pictures of nickel metals before experiment and after experiment