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SMALL SCALE PRODUCTION OF ZINC SULPHATE AND ITS APPLICATION

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Abstract

Zinc sulphate is a water soluble inorganic compound. It can be prepared by treating virtually any zinc containing material (metal, minerals, oxides) with sulfuric acid followed by evaporation and crystallization. Zinc and its alloys have been used as a protective and decorative coatings over a variety of metal substrates. In this research, commercial grade zinc oxide was used as raw material for the preparation of zinc sulphate. Moreover, a make-shift stainless steel reactor was constructed for the production of zinc sulphate. Prepared zinc sulphate was used in zinc electroplating process. The purity of zinc oxide was found to be 98.58(% w/w) by volumetric analysis method and 99.953 (%w/w) by EDXRF method. The maximum yield of zinc sulphate 79.50 (%w/w) was obtained by treating 10 g of zinc oxide with 75 mL of 3 M sulphuric acid. Prepared Zinc sulphate was identified by X-ray Diffraction (XRD) and the purity and composition was determined using Energy Dispersive X-ray Flourescence (EDXRF). 2 kg of zinc sulphate per batch was produced from 488 g of zinc oxide by using a make-shift stainless steel stirred tank reactor. Iron sheet was electroplated in the zinc sulphate solution using different parameters by varying the voltage, current and electroplating time. The acceptable bright colour and suitable thickness was obtained at 6V, 5A, 15 min electroplating time. The corrosion rate of selected zinc coated layer in artificially simulated environments (tap water, 3.5 % NaCl solution and dilute acid solution) and standard salt spray test (ASTM B 117) was also studied. The selected zinc coated layer give 72 hr protection for salt spray test. The surface morphology of the zinc coating before and after corrosion were studied by Scanning Electron Microscopy (SEM).

***Keywords*:** zinc sulphate , electroplating

Introduction

Zinc and its alloys have been used as a protective and decorative coatings over a variety of metal substrates for more than 100 years ago. It gives excellent corrosion resistance, particularly in industrial and urban environments. Zinc coating can be obtained by different techniques such as

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batch hot-dip galvanizing, continuous sheet galvanizing, zinc painting, zinc spray metalizing, mechanical plating, electrogalvanizing and zinc electroplating. Of these, zinc electroplating is the most prevalent for functional and decorative applications. Its relatively low cost makes the zinc plating process the top choice for affordable corrosion protection.(T.J Tuaweri et. al,2013) Typical zinc electroplating applications include coating nuts, bolts, washers and various automotive parts. Other common uses include the production of electrical transmission components and plating fasteners. (H.B. Muralidhara,2011) Three main types of zinc plating are being done today; cyanide zinc solution, chloride zinc solution and zinc sulphate solution. With the never-ending environmental pressures that are being placed on industry, there is a worldwide push to move away from cyanide zinc into chloride and sulphate plating. The toxicity and stringent regulation against water pollution and hence costly effluent disposal of cyanide based baths has led to the increased interest and accelerated growth of acid zinc based baths in the past few years. Many of the acid types bath utilize zinc sulphate and are used to electroplate cast iron and malleable irons.

Zinc electroplating is amenable to both rack plating or barrel plating processes. The former is preferable for providing suitable thickness distribution on larger or more complex parts. Barrel plating is recommended for coating smaller objects such as nuts and bolts.(Bamidele. MDurodala)

In this research, zinc sulphate was prepared from zinc oxide with sulphuric acid. Prepared zinc sulphate solution was used as a source of zinc in zinc electroplating bath to replace cyanide electroplating process which causes environmental impact. Electroplating of iron sheet was carried out by using prepared zinc sulphate solution as electrolyte under different conditions. The assessment of the quality of zinc coated sheets by different solutions were also studied. The main objective of this study was to produce zinc sulphate and to study the effective utilization of zinc sulphate in electroplating process in place of cyanide electroplating process.

Materials and Methods

Raw Materials

Zinc oxide (commercial grade), Iron Sheet (H 490143) were obtained from Khin Maung Nyunt Trading Co.,Ltd. South Dagon Township, Yangon Region. Analar grade chemicals (India) such as aluminium sulphate, boric acid, sulphuric acid, hydrochloric acid, chromic acid and sodium hydroxide were purchased from Golden Lady Chemical Sale Centre, Pabedan Township, Yangon Region. Distilled water and deionized water were obtained from Department of Industrial Chemistry, Dagon University.

Methods

Preparation of Zinc Sulphate from Zinc Oxide

Effect of Volume of 2M H_2SO_4 on Yield Percent of Zinc Sulphate

65 mL of 2 M sulpuric acid was placed in a 250 mL beaker. 10 g of zinc oxide powder was added and stirred with a magnetic stirrer at 100 rpm for 10 min to dissolve all of the zinc oxide powder. When the zinc oxide powder was completely dissolved, the solution was heated at 70ºC in a water bath for 30 min. After the precipitation of zinc sulphate, the solution was filtered. After that saturated zinc sulphate solution was cooled down to room temperature and left for 2 days. Zinc sulphate was filtered and washed with 30 mL of ethanol and dried in a desiccator. Yield percent of zinc sulphate was calculated as follows:

$$\text{Yield of zinc sulphate, \%} = \frac{\text{experimental weight of the product}}{\text{theoretical weight of the product}} \text{ x } 100$$

Other experiments were conducted by the above procedure but by varying the volumes of sulphuric acid (70 mL, 75 mL and 80 mL) were used. The results are shown in Table (1).

Effect of Strength of H_2SO_4 on Yield Percent of Zinc Sulphate

The same procedure as described in the above experiment was carried out using 75mL of sulphuric acid at the various concentrations of 3M and 4M. The results are shown in Table (2).

Construction of Reactor Design for Production of Zinc Sulphate

A make-shift stirred tank reactor was constructed based on the amount of zinc sulphate crystals to be prepared. The inner tank (304 grade stainless steel) was surrounded by outer layer (202 grade stainless steel) with the water jacket between them. The impeller was inserted at the centre of the inner tank which was connected to the 15W DC electric motor for agitation. Electric heater (1000 W) was used to heat water and zinc sulphate solution. Digital thermometer was used to measure the temperature of zinc sulphate solution thoroughout the experiment until the completion of reaction.

The volume of the reactor was (346.185 in^3) and size of agitator (1.77 in D, 7.5 in length) was made of 304 grade stainless steel. It was fabricated at Shwe Family Equipment and Metal Moulding, Company. No (198C), Sintae St., Industrial Zone(3),South Dagon Township, Yangon. Maximum yield of zinc sulphate 2 Kg per batch was obtained by using 488 g of zinc oxide.

Electroplating of Iron Sheet
Preparation of Electrolyte Solution

Distilled water 8.5 L was poured into a container and other ingredients such as 2400 g of zinc sulphate, 300 g of aluminium sulphate, 300 g of boric acid were added with agitation to enhance complete dissolution. The solution was finally made up to 10 L by adding distilled water.

Pretreatment of Iron Sheet for Electroplating

The iron sheets were cut into pieces of 80.32 cm^2. They were punched in machine and washed with detergent to remove any grease and oil adhering on the iron sheet and then washed with water. After that, the sheets were pickled in 6M hydrochloric acid for 5 min to remove scales and rust and then brushed with iron brush. After acid pickling, the iron sheets were washed again with water to remove traces of acid and dried in an oven and weighed.

Electroplating of Iron Sheet

In electroplating bath, two pure zinc plates were used as anodes. The pre-weighed iron sheet 80.32 cm^2 already attached to the flexible copper wire was hanged at the cathode of the zinc electroplating bath. Both anodes and cathode were dipped in the electrolyte solution containing zinc sulphate when a direct current was passed through the electrolyte, zinc ions were plated onto the iron cathode. The whole process was carried out at room temperature. Electroplating process was carried out at different electric voltages such as (3V, 4V, 5V,6Vand 7V), electroplating time (5 min, 10 min, 15 min and 20 min) at electrodes distances of 12.7cm. After electroplating, zinc coated iron sheet was removed and rinsed with water, then it was dipped in sodium chromate solution to fix the zinc layer for 5 sec and then washed with water and caustic soda solution. Finally, it was washed with water again and dried in an oven for 5 min. Zinc coated iron sheet was obtained and weighed again.

Results and Discussion

The purity of zinc sulphate to be used in electroplating process is important. Therefore, the purity of zinc oxide was examined both by volumetric analysis and EDXRF. The purity of zinc oxide was 98.58% by volumetric method (ASTM E 56) and 99.953 % by EDXRF. The XRD result of zinc oxide is shown in Fig. (1). From Tables (1) and ( ), a high yield 79.50(%w/w) of zinc sulphate was obtained by using 10 g of zinc oxide with 75 mL of 3 M sulphuric acid. Although the concentration of sulphuric acid was increased up to 4 M, the yield percent of zinc sulphate did not increase considerably. XRD spectrum shows the high purity of prepared zinc sulphate sample. The composition of the commercial grade, analar grade and prepared zinc sulphate were determined by EDXRF. The content of zinc in prepared zinc sulphate is higher than commercial grade but lower than that of the analar grade. The results are shown in Fig. (8), (9) and (10).

Zinc sulphate is the primary component for zinc ion in electrolyte solution. Aluminium sulphate was used to give a bright deposit on the substrate. Apart from bright deposit, aluminium sulphate gave good adhesion of metal on the surface of the substrate. It was also used to improve the uniformity of deposition of zinc on iron sheet. One of the most important additives in an electroplating bath was boric acid which serves as a weak buffer to control the pH and to give a smooth deposit. The elemental composition of electrolyte solution was examined by EDXRF. The respective spectra is shown in Fig. (10).

Zinc electroplating process was studied by varying the electroplating parameters such as voltage, current and electroplating time. The effect of voltages (3V,4V,5V,6V and 7V) on thickness of zinc coating on iron sheet at different electroplating times (5 min, 10 min,15 min and 20 min) are shown in Table (3). Electroplating at low current and voltage takes longer electroplating time to obtain a certain thickness. The deposited zinc increased with the increase in voltage (3 V to7 V) but gray colour appears at high voltage and electroplating time longer than 15 min. Bright silvery colour and smooth surface was obtained at 6 V and electroplating time of 15 min. Beyond these process conditions, rough coated zinc layer or burning occurred on the iron sheet.

The quality of the best parameters of zinc electroplated sheet was assessed by the resistance in artificially simulated environments. Tap water (pH=6.7), 3.5 % NaCl solution (pH=6.5) and dilute sulphuric acid solution (pH= 5.3) were used as corrosion medium. The corrosion rate of electroplated sample by different environments are shown in Table (4). From these results, the corrosion rate of zinc electroplated sample increased with increasing treatment time in all the different environments. During 60 days, the corrosion rate of zinc coating in sodium chloride solution was faster than in sulphuric acid solution and tap water.

In NaCl solution, the corrosion rate of zinc coating was the highest in the first 15 days due to the dissolution of zinc followed by passivation of an impermeable film (Redox reaction) on the intended metal surface and no rusting occurs for a test period of 60 days. The corrosion resistance of zinc coating to the neutral salt spray test was also conducted by using (ASTM B117) method. The number of hr for the formation of white rust on zinc layer indicated the corrosion resistance. In the present case, selected zinc coated sheet produced white rust after 72 hr treatment. Zinc coated sample could be used in various environments according to the salt spray test period of 72 hr. The surface morphology of the deposited zinc layer before and after corrosion tests are shown in Fig. (12).

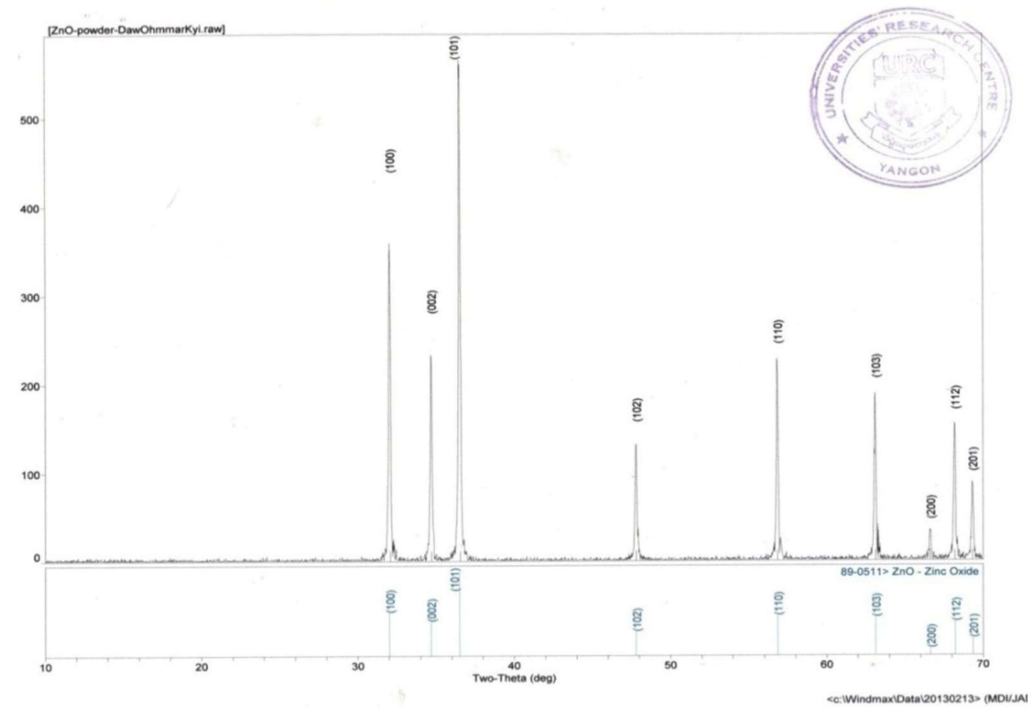

Figure 1. XRD Spectrum for Zinc Oxide

Table 1: Effect of Volume of 2M Sulphuric Acid on Yield of Zinc Sulphate from Zinc Oxide

Evaporation time at 70°C = 30 min
Reaction time = 10 min
Weight of zinc oxide = 10 g

Sr. No.	Reaction Time (min)	Rate of Agitation (rpm)	Concentration of H_2SO_4 (M)	Volume of H_2SO_4 (mL)	Yield Percent of $ZnSO_4$ (% w/w)
1.	10	100	2	65	71.51
2.	10	100	2	70	73.45
3.	10	100	2	75*	78.47
4.	10	100	2	80	78.49

* The most suitable condition.

The experiments were conducted at the Department of Industrial Chemistry, Dagon University.

Table (2) Effect of Strength of Sulphuric Acid on Yield of Zinc Sulphate From Zinc Oxide

Evaporation time at 70°C = 30 min
Reaction time = 10 min

Sr. No.	Reaction Time (min)	Rate of Agitation (rpm)	Concentration of H_2SO_4 (M)	Volume of H_2SO_4 (mL)	Yield Percent of $ZnSO_4$ (% w/w)
1.	10	100	2	75	78.47
2.	10	100	3*	75	79.50
3.	10	100	4	75	79.51

* The most suitable condition.

The experiments were conducted at the Department of Industrial Chemistry, Dagon University.

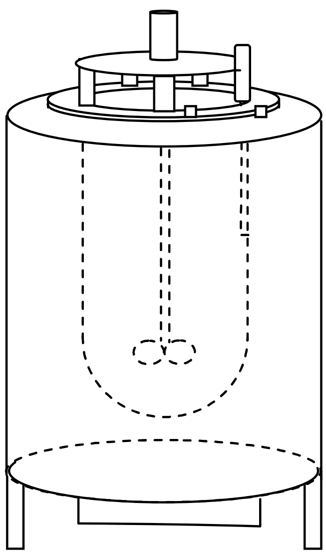

Figure 2: Schematic Diagram of Stirred Tank Reactor for the Production of Zinc Sulphate

Figure 3: Stirred Tank Reactor for the Production of Zinc Sulphate

Figure 4: Zinc Oxide (Commercial grade)

Figure 5: Prepared Zinc Sulphate

Figure 6 : Zinc Coated Iron Sheet

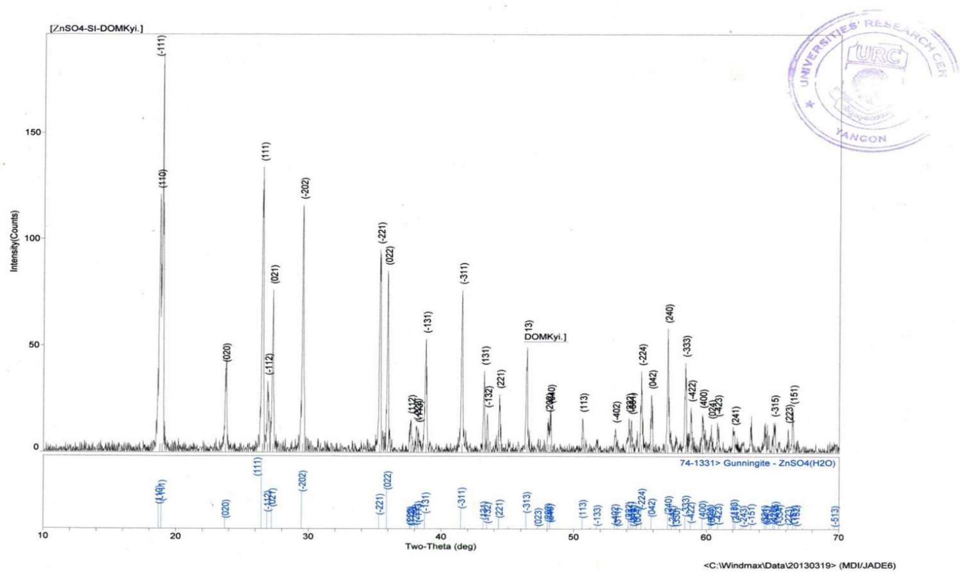

Figure 7: XRD Spectrum of Prepared Zinc Sulphate

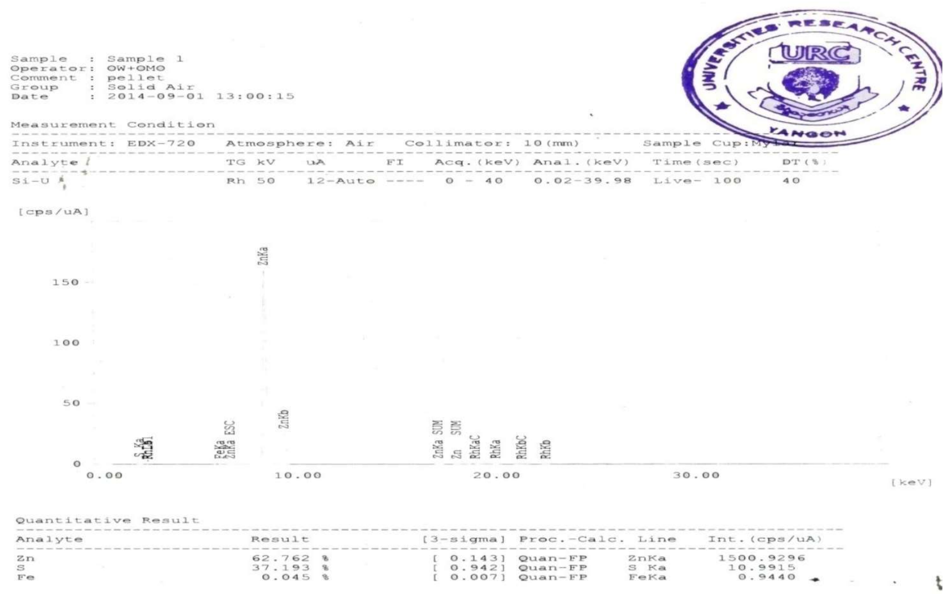

Figure 8: EDXRF Results of Prepared Zinc Sulphate

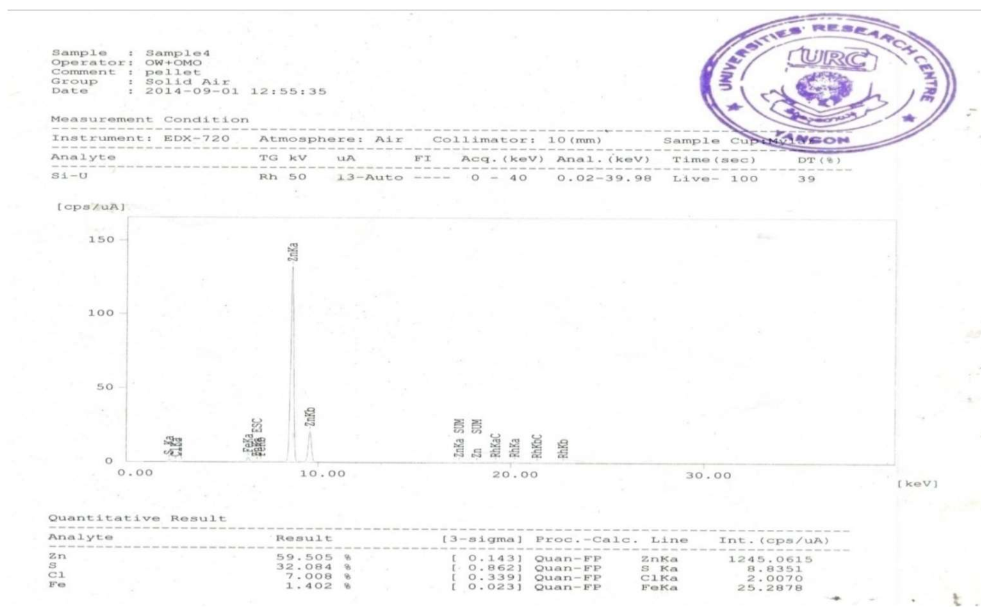

Figure 9: EDXRF Results of Zinc Sulphate (Commercial grade, India)

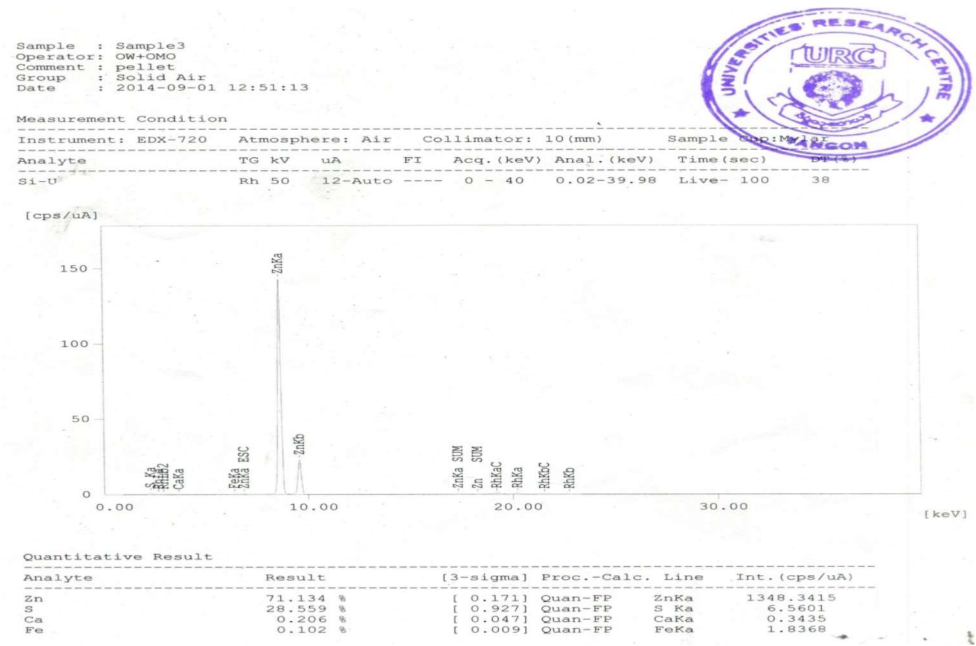

Figure 10: EDXRF Results of Zinc Sulphate (Analar grade, India)

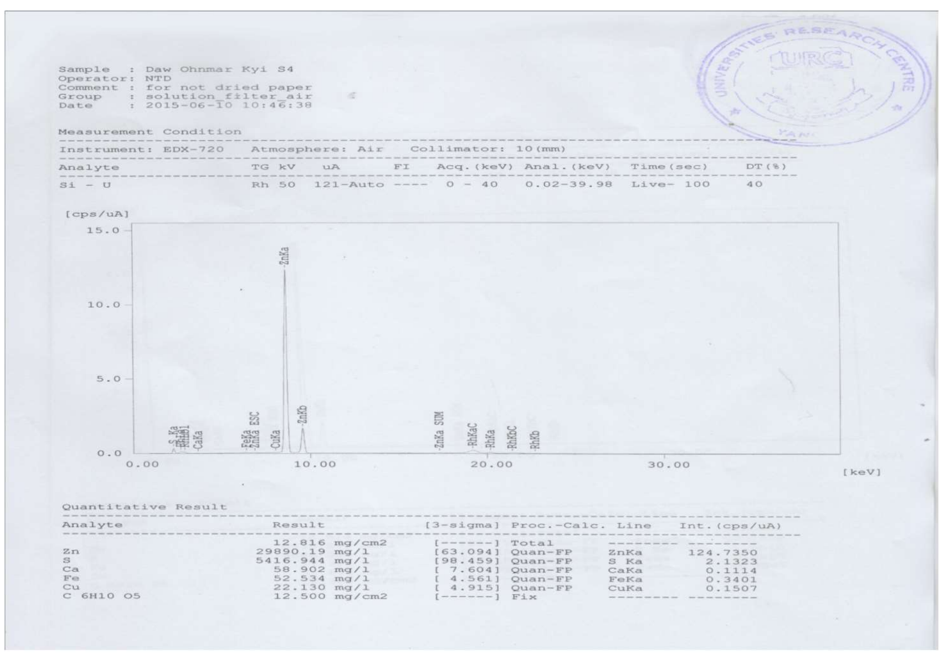

Figure 11: EDXRF spectrum of Electrolyte Solution

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Table 3: Effect of Voltage on Thickness of Zinc Coating on Iron Sheet at Various Electroplating Time

Thickness of iro ... n electrodes = 12.7 cr

Sr. No.	Electric Voltage (V)	Electric Current (A)	Actual												Zinc Coated Lay Service Conditi							
			5 min	10 min	15min	20 min	5 min	10 min	15min	20 min	5 min	10 min	15min	20 min	5 min	10 min	15min	20 min	5 min	10 min	15min	20 min
1.	3	2	3.14	6.62	9.73	14.06	3.54	7.09	10.63	14.18	B	B	B	B	<SC 1	SC 1	>SC 2	>SC 3	S	S	S	S
2.	4	3	4.72	10.39	14.53	19.37	5.32	10.63	15.95	21.27	B	B	B	B	<SC 1	>SC 2	>SC 3	>SC 3	S	S	S	S
3.	5	4	6.29	10.85	20.44	25.44	7.09	14.18	21.27	28.35	B	B	B	B	>SC 1	>SC 2	>SC 3	SC 4	S	S	S	R
4.	6*	5	7.87	16.71	23.57*	34.07	8.86	17.73	26.59	35.43	B	B	B	B	>SC 1	>SC 3	>SC 3	>SC 4	S	S	S	R
5.	7	6	10.31	20.29	29.63	-	10.63	21.27	31.90	-	B	B	B	-	>SC 2	>SC 3	>SC 4	-	S	SR	R	-

The experiments were conducted at KMN Manufacturing Co.,Ltd.South Dagon, Yangon Region *The most suitable condition. **T.J.Tuaweri et.al , A Study of Process Parameters for Zinc Electrode position from a Sulphate Bath, 2013. (Faraday's Law of Electrolysis) B = Bright Silvery Colour, S=smooth , SR=slightly rough, R=rough

Classification of Thickness Class for Electrodeposited Coatings of Zinc on Iron and Steel (ASTM B 633)

Service Condition	Thickness, min (µm)
SC 4 (very severe)	25
SC 3 (severe)	12
SC 2 (moderate)	8
SC 1 (mild)	5

Examples of Appropriate Service Conditions and Description of Service Conditions

SC 4 (Very Severe) - Exposure to harsh conditions, or subject to frequent exposure to moisture, cleaners, and saline solutions, plus likely damage by denting, scratching, or abrasive wear. e.g: plumbing fixtures, pole line hardware.

SC 3(Severe) - Exposure to condensation, perspiration, infrequent wetting by rain, and cleaners. e.g: tubular furniture, insect screens, window fittings, builder's hardware, military hardware, washing machine parts, bicycle parts.

SC 2(Moderate) - Exposure mostly to dry indoor atmospheres but subject to occasional condensation, wear, or abrasion. e.g: tools, zippers, pull shelves, machine parts

SC 1 (Mild) - Exposure to indoor atmospheres with rare condensation and subject to minimum wear or abrasion. e.g: buttons, wire goods, fasteners.

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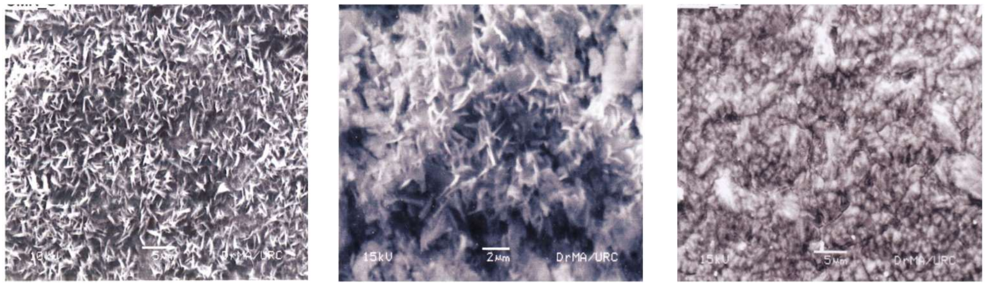
Table 4: Change in Appearance, Colour and Weight Loss of Zinc Coating on Iron Sheets After Treatment in Artificially Simulated Environments
Thickness of z

Artificially Simulated Environments	Zinc Coat on Iron Sheet Before Treatment	Zinc Coating on Iron Sheet After Treatment											
		15 days			30 days			45 days			60 days		
	colour and surface appearance	wt. loss of zinc (% w/w)	colour	surface appearance	wt. loss of zinc (% w/w)	colour	surface appearance	wt. loss of zinc (% w/w)	colour	surface appearance	wt. loss of zinc (% w/w)	colour	surface appearance
Tap Water	silvery white, smooth	0.074	silvery white	smooth	0.156	silvery white	smooth	0.216	silvery white	smooth	0.232	silvery white	smooth
3.5 % NaCl Solution (pH=6.5)	silvery white, smooth	2.23	silvery white	white rust on surface	6.15	gray	corroded surface	9.35	gray	corroded surface	12.21	gray	corroded surface
Dilute Sulphuric Acid Solution (pH= 5.3)	silvery white, smooth	0.19	silvery white	white rust on surface	1.24	silvery white	corroded surface	2.63	gray	corroded surface	4.25	gray	corroded surface

The experiments were carried out at the Department of Industrial Chemistry, Dagon University.



(a) Bright Silvery Colour of Zinc Coat (60 days)

(b) Deterioration of Zinc Coat after Treatment with 3.5 % NaCl Solution (60 days)

(c) Deterioration of Zinc Coat after Treatment with Acid Solution (60 days)

Figure 12: SEM Micrograph for Morphology of Zinc Coated Iron Sheet

Conclusion

In this research, zinc oxide (commercial grade,China) which has a purity of 99.953 % obtained from KMN Manufacturing Co., Ltd. was used to produce zinc sulphate. The maximum yield of zinc sulphate 79.50 (% w/w) was obtained by using 10g of zinc oxide with 75 mL of 3 M sulphuric acid. Analysis by X-ray Diffraction (XRD) method shows the purity of the prepared zinc sulphate which is the same as the technical grade zinc sulphate. Based on the required amount of zinc sulphate, make-shift stirred tank reactor was constructed. Maximum yield of zinc sulphate 2 Kg per batch was obtained by using 488 g of zinc oxide. Prepared zinc sulphate was used in the preparation of electrolytes solutions for zinc electroplating. The best operating conditions were 6V, 5 A, 15 min electroplating time at distance between electrodes of 12.7 cm. From salt spray test, it can be observed that the prepared zinc coated iron sheet resists up to 72 hr using salt spray test method according to ASTM B117.Therefore zinc coated iron sheet with selected parameters can be used in various environments.

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