

NANOCERAMIC COATINGS – SYNTHESIS, CHARACTERIZATION AND THEIR APPLICATIONS

Presented by

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Overview



1. Introduction
2. Experimental
3. Research & Discussion
4. Summary & Conclusion

**Metal Finishing Purposes
Decorative, Protective, Functional**



Anticorrosion

Antifouling



1. Introduction

Objectives

1. To develop and characterize Nanozirconia coating chemical as metal pretreatment base coat for anticorrosive applications
2. To synthesize & characterize hexafluoro zirconic acid powder
3. To characterize Nanozirconia coating (NZ) on different metal components – MS, GI, Al, Cu.
4. To synthesize & characterize nano copper in polyurethane top coat for antifouling applications on MS, GI, Wood and Cement panels

Novelty of Present Work

- Powder form of hexafluoro zirconic acid synthesized
- H_2ZrF_6 used in nano-zirconia base coat
- Applied on Metals - Cu, MS, GI and Al
- Applied on Non-metals – Wood, Slate stone, Cement panels
- Nano copper, nano zinc in organic top coats
- Antifouling properties with the least leaching
- Nano zinc spot welding primer with epoxy resin
- 50 Years old Temple Kalasams nanocoated

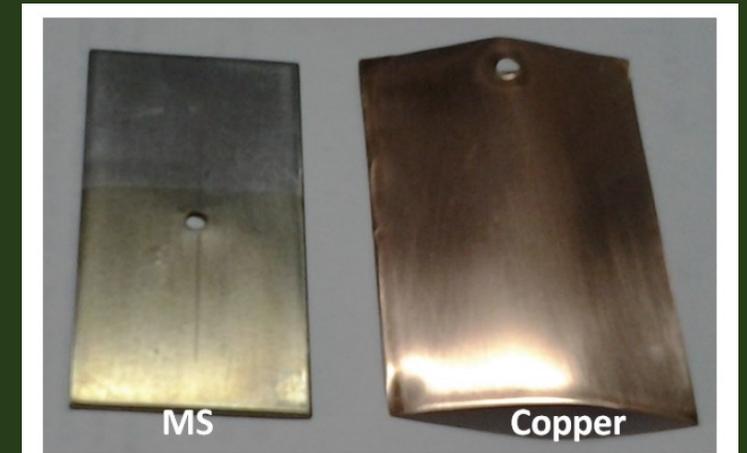
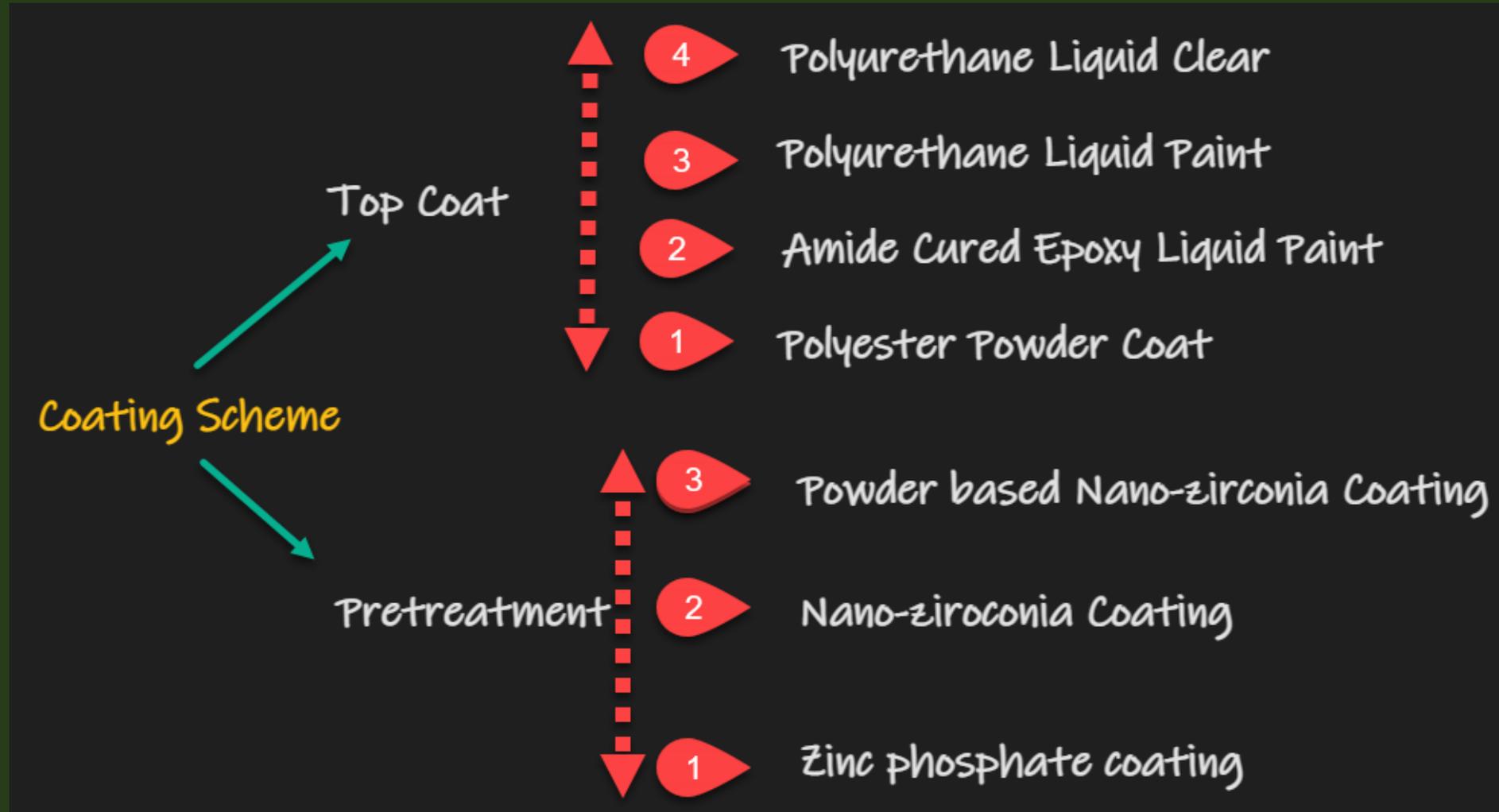


Fig. 41 Nanozirconia coating on MS and Cu



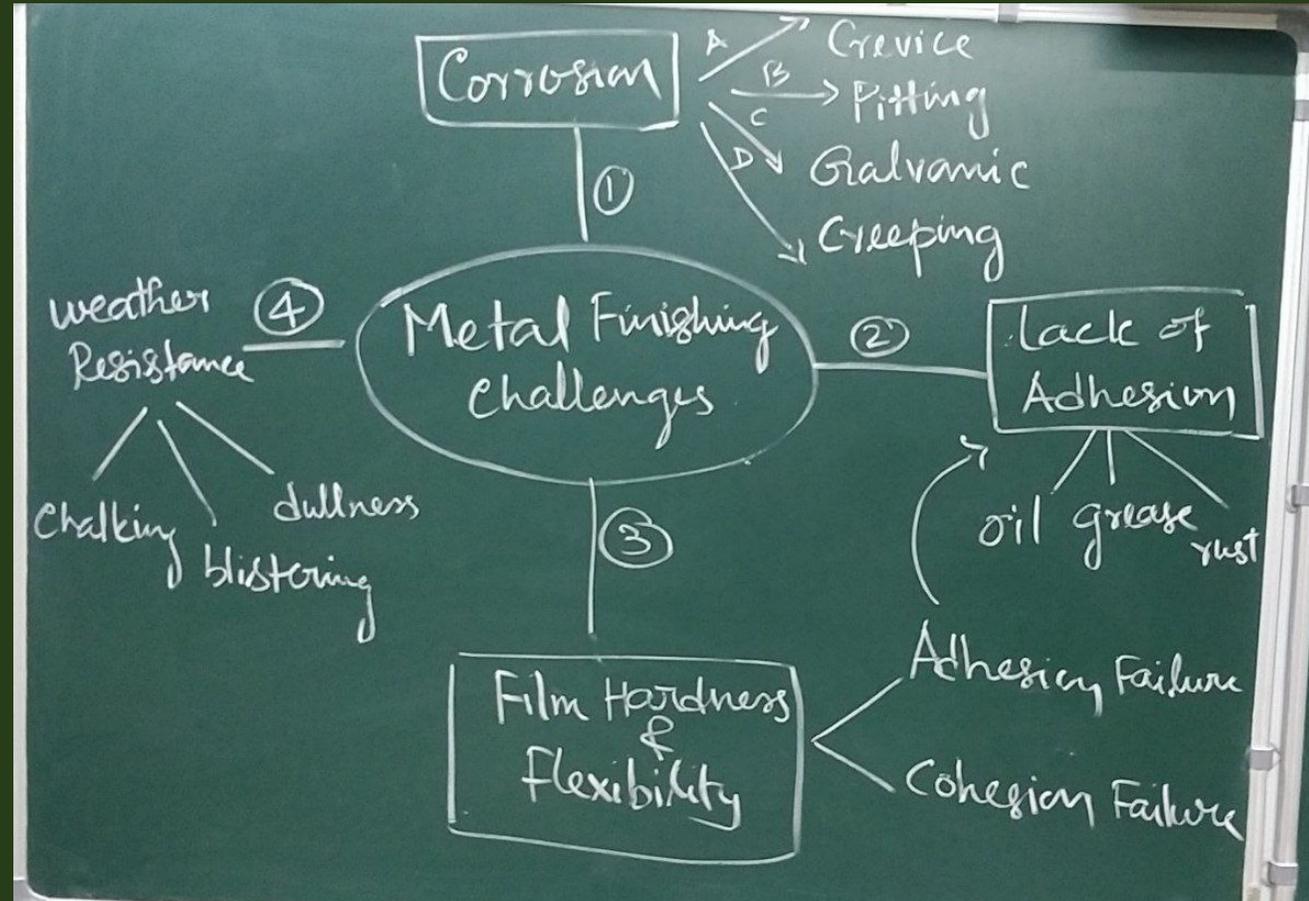
Coating Scheme



Condition of Sheet Metal Components

- Corrosions

- Crevice - by stagnant electrolyte trapped
- Pitting - prolonged contact with the corrosive acids
- Galvanic - dissimilar metals are in contact with each other
- Creeping corrosions - visible on scratches of paint layer coated, also called cosmetic correction [Sato et al]



ZnP vs NZ (Nano Zirconia) Coating Stages

ZnP

1. Alkaline degreasing
2. Double Water rinse
3. Zinc Phosphating at 55° C
4. DM Water Rinse
5. Chromic passivation *
6. Hot air blow / oven drying

Note: Proper use of additives such as nitrites refine the ZnP coating (Sankaranarayanan)

NZ

1. Alkaline Decreasing
2. Double Water Rinse
3. DM Water Rinse
4. NZ Coating at RT
5. DM Water Rinse
6. Hot air blow / oven drying

ZnP vs NZ Features

ZnP

1. Crystalline
2. Soft (nail marks), matt
3. Microporous and anchoring
4. Opaque
5. Grey
6. Hot immersion / spray
7. Process time: 3 – 5 min
8. Sludge disposal cost [Ghali et al] and environmental issue



NZ

1. Amorphous
2. Hard (no nail marks), glossy
3. Nanoporous and anchoring
4. Transparent
5. Gold lacquer
6. RT Immersion / Spray
7. Process time: 30 – 60 s
8. No sludges – lower cost and ecofriendly



Antifouling Coatings

- To retard fouling on ship hulls
- The colonization of bacteria
- Followed by growth of algae, fungi and barnacles
- Surface damage
- Affects the speed
- Increases the fuel consumption



Different Antifouling Coatings

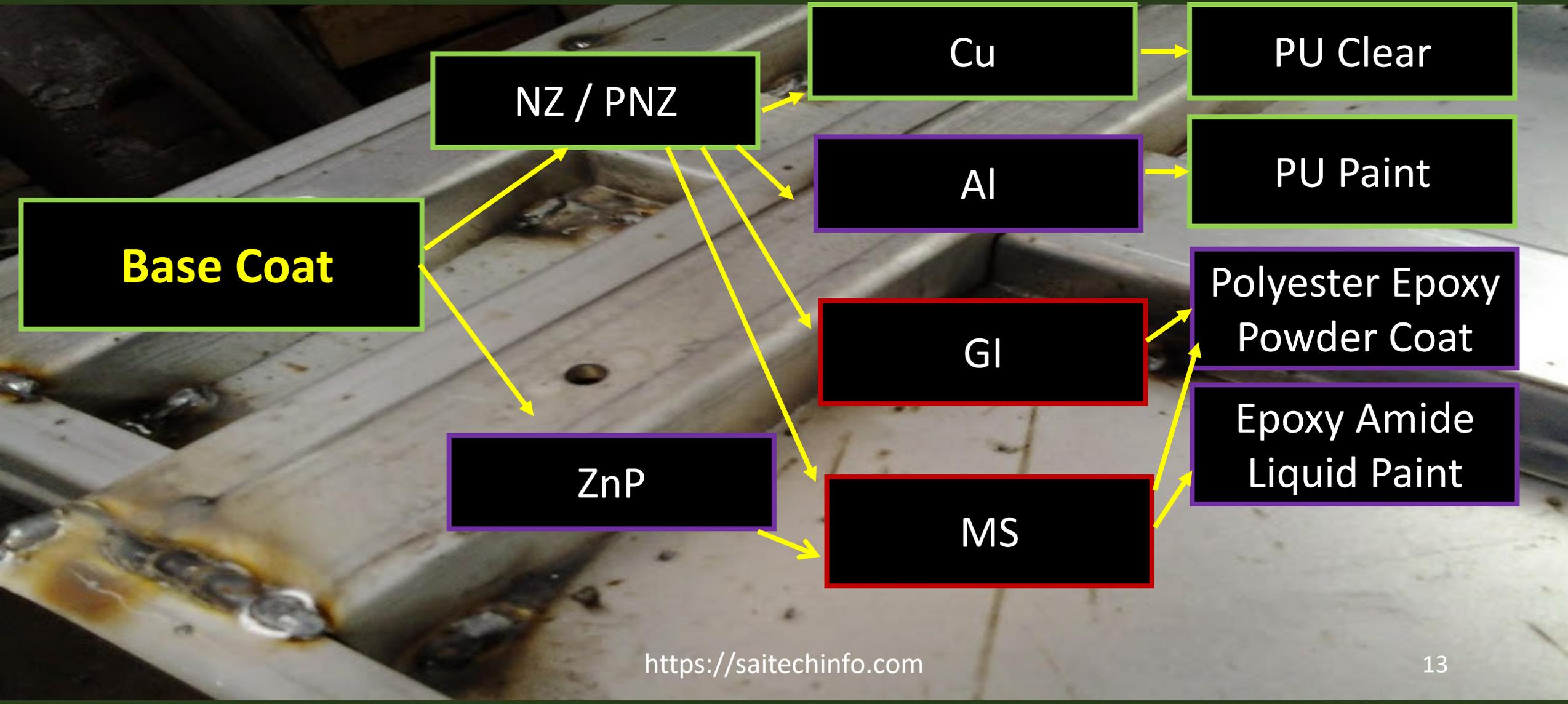
- Biocides - tributyl tin oxide, lead, arsenic, copper, tar and wax.
- Leaching issue - International maritime organization banned in 2003 the use of such biocides that affect the aquatic life (flora and fauna)
- Surface protection only without leaching





2. Experimental

2. Experimental – Anticorrosive Studies



Characterisation of Base Coats & Top Coats

Characterization of Base Coat

- Atomic Force Microscope (AFM)
- GE X-ray diffractometer (XRD)
- X-ray photoelectron Spectrometer (XPS)
- Field emission scanning electron microscope (FESEM)
- Electrochemical Impedance Spectroscopic Studies

Dry Film Characteristics of Top Coat

ASTM Methods

(American Society for Testing and Materials)

- B-117 - Neutral salt spray (NSS) resistance
- D-2247 - Humidity resistance
- D-2794 - Impact resistance
- D-3359 – Adhesion test

Cell Set up in EIS

- Working Electrode - the treated and untreated metal panels of 75 mm x 10 mm x 1 mm dimension without top coat paints, with each of them having 1 cm² exposed surface area
- Reference Electrode - Saturated calomel electrode
- Counter Electrode - Platinum wire
- Electrolyte - 3.5 % NaCl solution
- The polarization plots obtained in the potential range between -250 and +250 mV



Electro Chemical Studies

Corrosion rate measured by

- Polarization curves
- Linear polarization resistance
- Open circuit potential
- AC impedance measurement
- Electrochemical noise measurement
- Weight loss measurement.
- The electrochemical impedance measurements
- Scanning range of 0.1 Hz to 100 kHz.
- The electrochemical characteristics of the NZ coating with and without top coat
- Nyquist and Bode plots at their open circuit potentials.

Corrosion Rate

- Tafel polarization analyses carried out by extrapolating anodic and cathodic curves to the potential axis.
- The corrosion rate (CR) in mills per year (mpy) of the base coat calculated from corrosion current (I_{corr}), equivalent weight (EW) and density (d) of the corroding species.
- Corrosion current density (I_{corr}) was calculated from anodic (α) and cathodic Tafel coefficients (β).

$$CR(mpy) = \frac{0.13 \times I_{corr} \times EW}{d}$$

$$I_{corr} = \frac{\alpha\beta}{2.3(\alpha + \beta)} \times \frac{1}{R_p}$$

Porosity of the Coating

- R_p' = Polarization resistance of the untreated MS panel
- R_p = Polarization resistance of the treated MS panel
- $\Delta E_{corr} = E'_{corr} - E_{corr}$
- E'_{corr} = Corrosion potential of the untreated panel
- E_{corr} = Corrosion potential of the NZ treated MS panel
- α = Anodic Tafel coefficient

$$P = \frac{R_p'}{R_p} \times 10^{-\left(\frac{\Delta E_{corr}}{\alpha}\right)}$$

Preparation of NZ Conversion Coating Chemical

S No.	Raw materials	Quantity (g)	Remarks
1	DM water	46.0	Use deionized water only
2	Polyacrylic acid	4.0	25% solution in DM water Mix thoroughly using a mechanical stainless steel stirrer
3	Hexafluoro zirconic acid	5.0	45% solution in DM water Mix thoroughly
4	DM water	45.0	Use deionized water only
	Total	100.0	NZ chemical solution

PNZ – powder based nano-zirconia coating

Synthesis of H_2ZrF_6 and PNZ Coating

- Zirconia mixed with 48% HF
- Vigorously stirred for 12 h in a **PTFE beaker** in a **fume cupboard**
- Water soluble Zirconic acid formed + insoluble **white residue**.
- Miscible with polyacrylic acid solution
- Makes the metal pre-treatment very easy.
- The handling and transport much easier and safer than liquid form
- PNZ bath made up and coated on Metals.

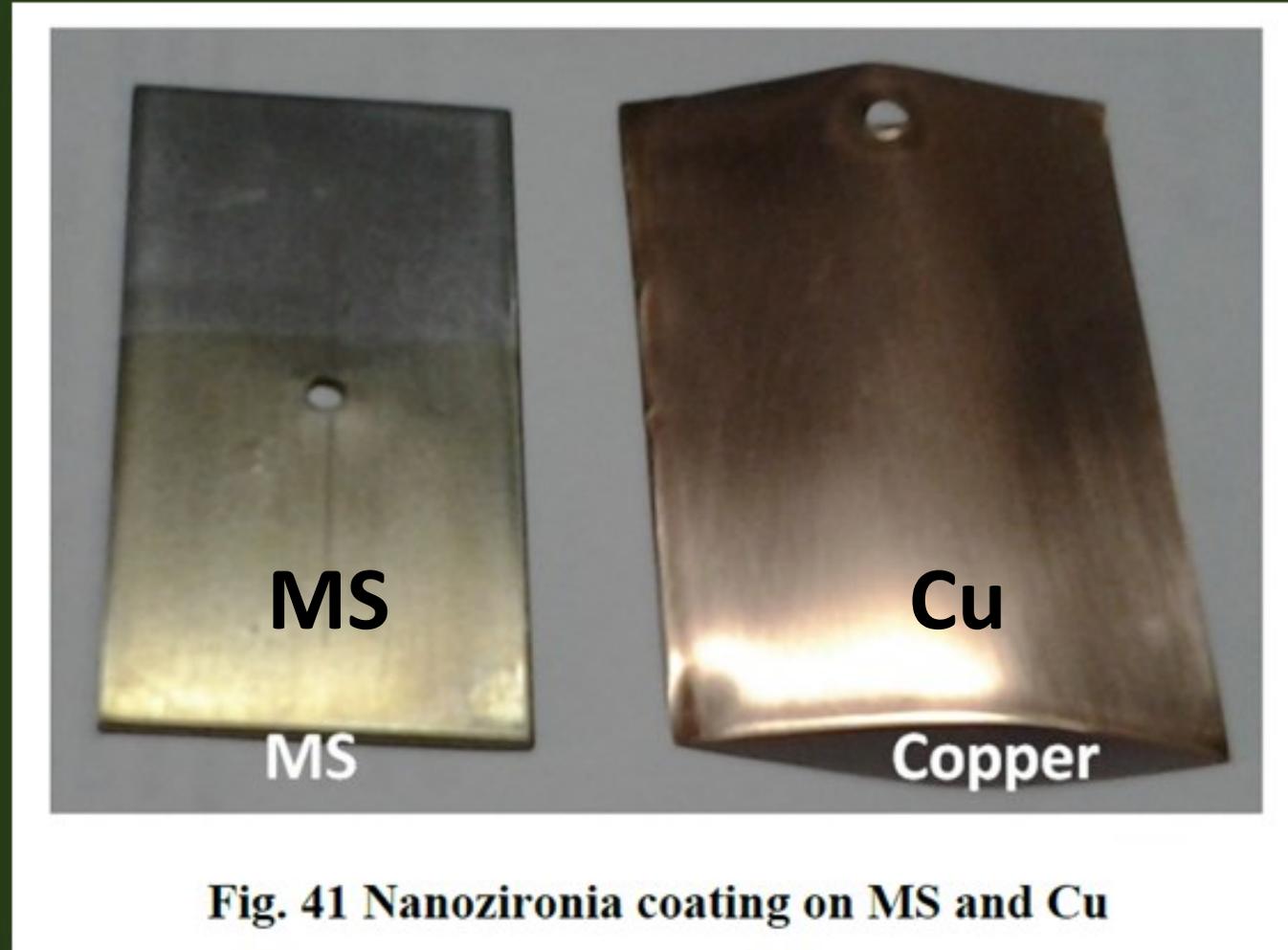
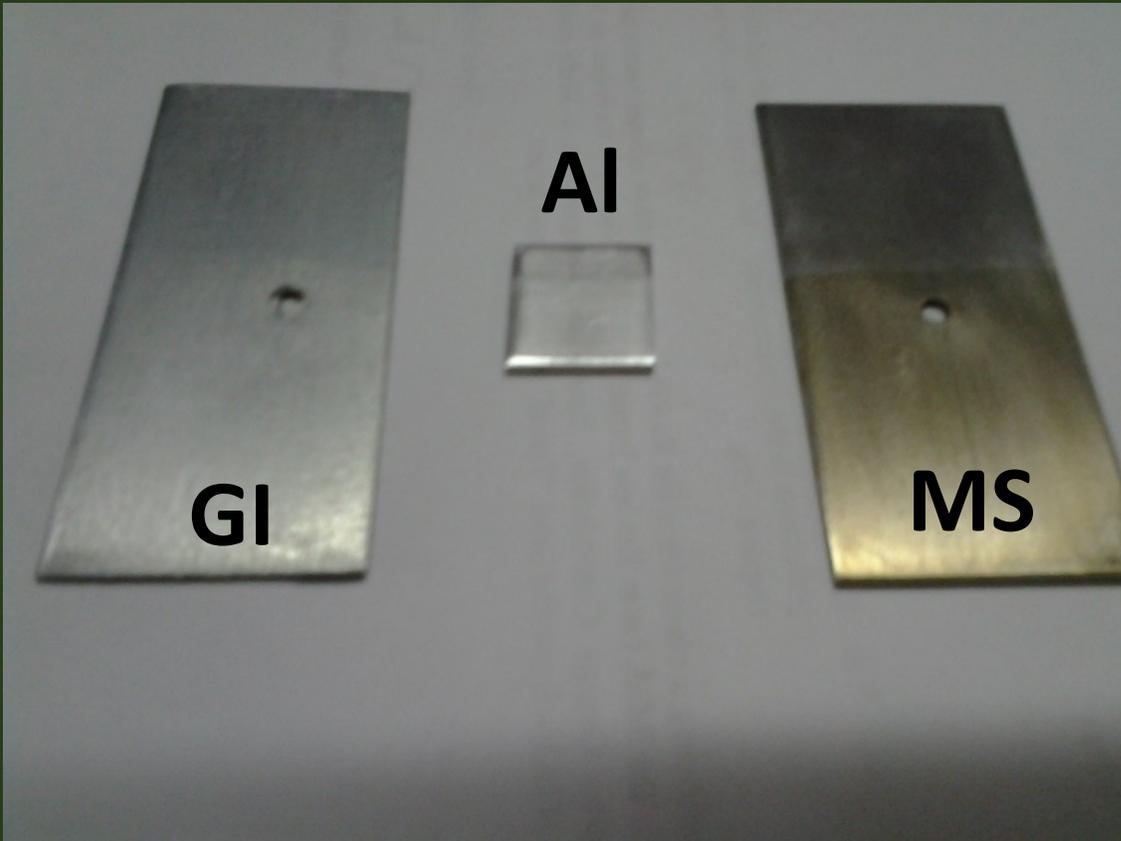
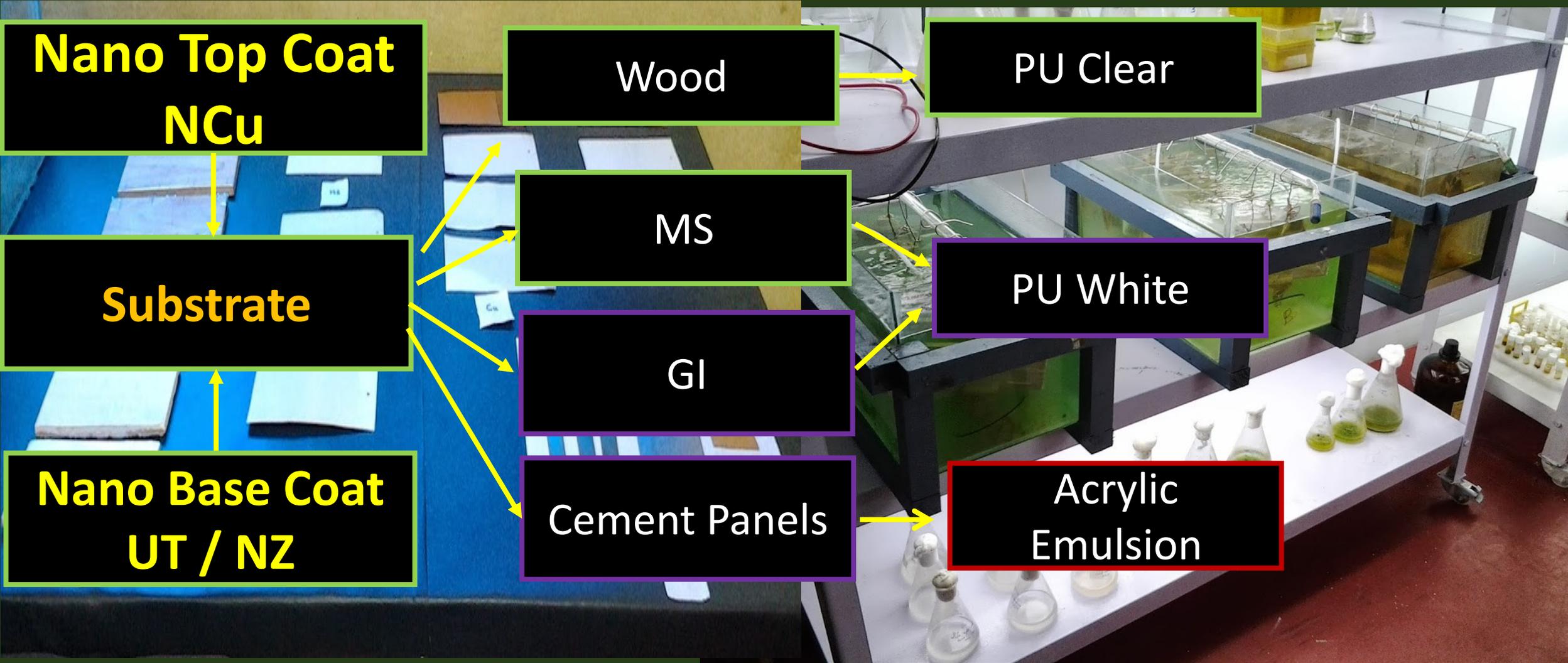


Fig. 41 Nanozirconia coating on MS and Cu

PNZ Coat applied on various Metal Panels



Antifouling Studies



3 Tanks with 3 Types of Algae

A. *Arthrospira platensis*

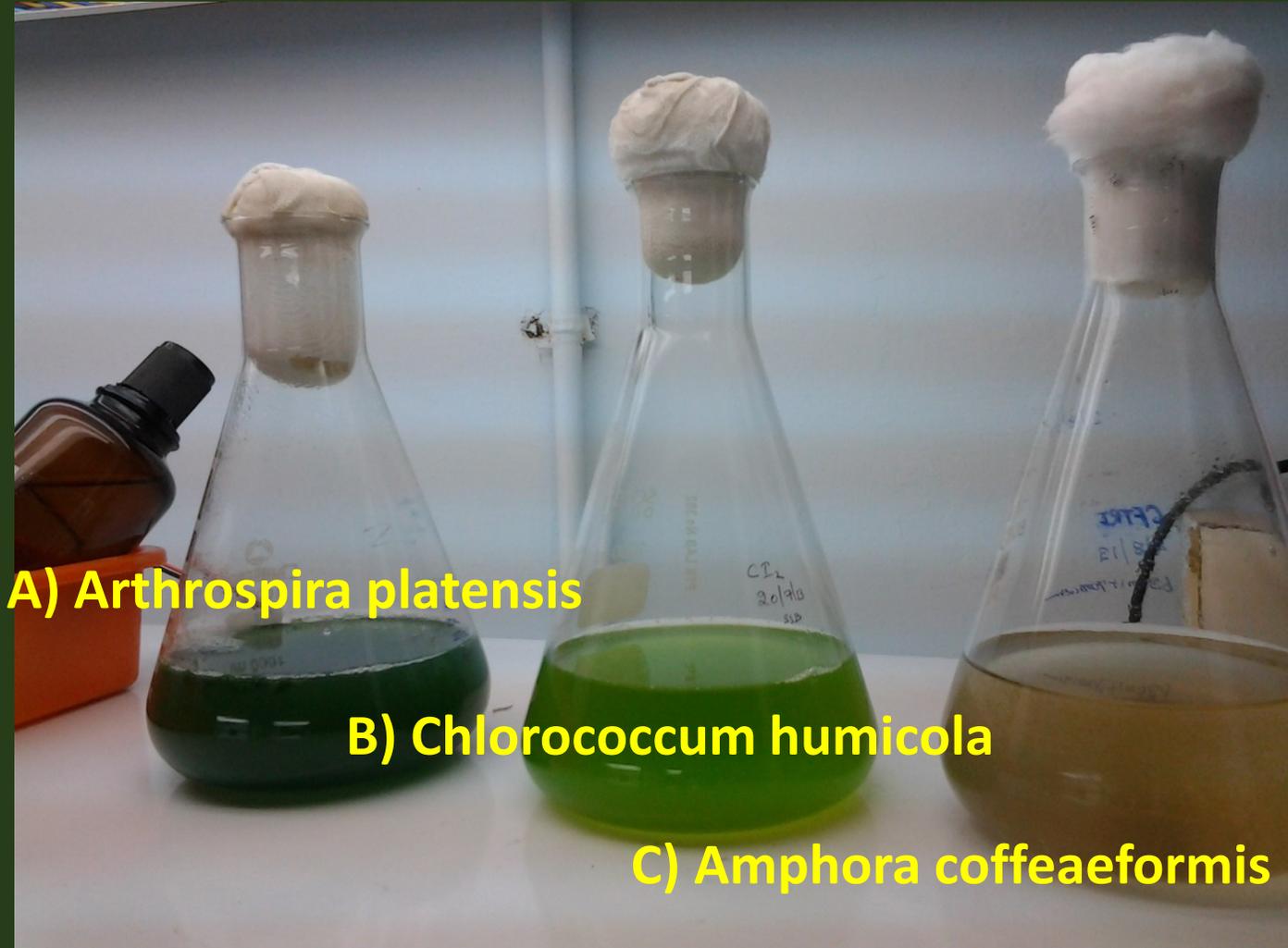
- Habitat - tropical and subtropical water bodies
- Zarrouk's medium (MgSO_4 , CaCl_2 , FeSO_4 , other nutrients)

B. *Chlorococcum humicola*

- freshwater and marine water
- Basal medium (CaCl_2 , MgSO_4 , KCl , NaHCO_3 , $\text{NaH}(\text{PO}_4)_2$, amino acids, vitamins)

C. *Amphora coffeaeformis*

- marine water
- F/2 medium – (B12, Biotin, Thiamine)



A) *Arthrospira platensis*

B) *Chlorococcum humicola*

C) *Amphora coffeaeformis*

Coated Wooden and Cement Panels

NCu

Bare

NCu

Bare



Fig. 61 Wooden Panels kept in (A) *Arthrospira platensis*; (B) *Chlorococcum humicola*; (C) *Amphora coffeaeformis*. L: Nano-treated panels, R: Control panels

Fig. 60 Cement Panels kept in (A) *Arthrospira platensis*; (B) *Chlorococcum humicola*; (C) *Amphora coffeaeformis*. L: Nano-treated panels, R: Control panels

Coated MS Panels

- Cu leached out from the nano Cu composite paint coated panels – in the lowest level
- Measured by ICP spectrometry
- 10 mL of bulk tank-3 solution made up to 50 mL at different time intervals (10, 20 and 30 days).
- These solutions analyzed for copper leached out from the nano top coat.

NCu

Bare

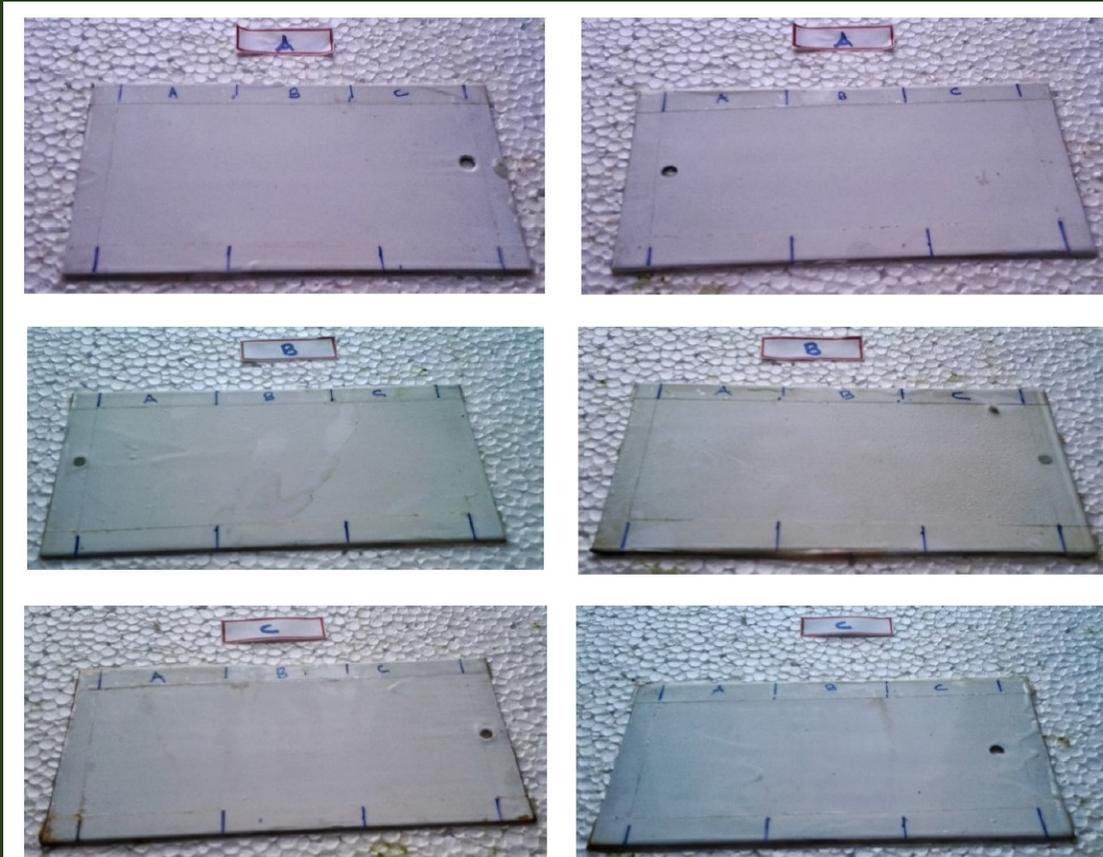
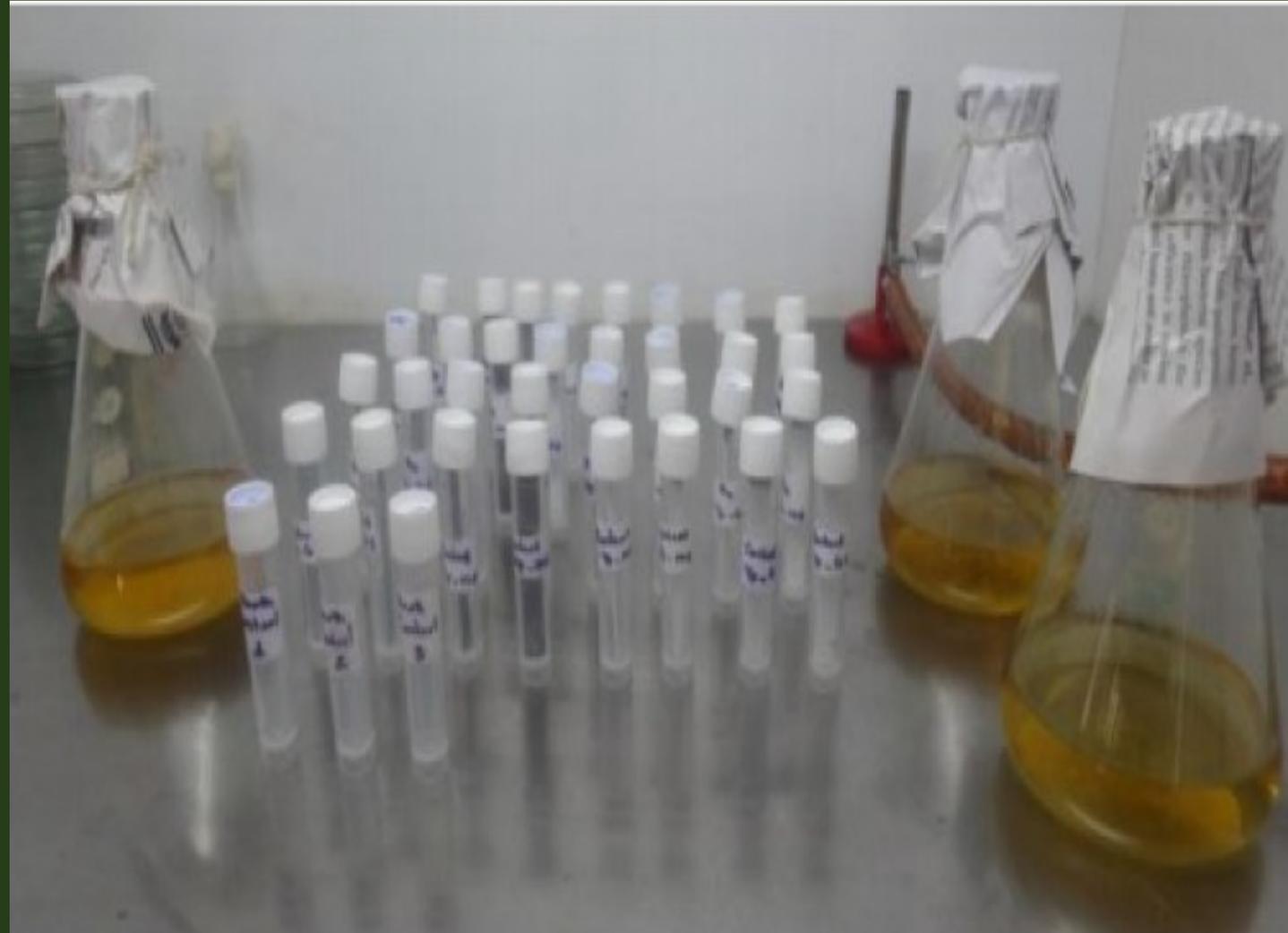
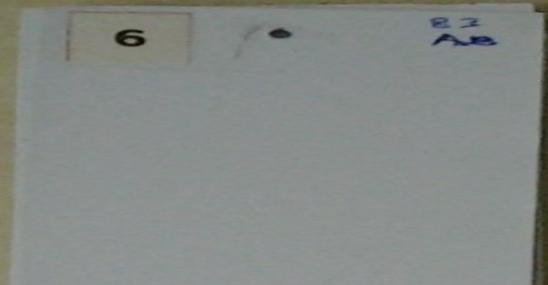
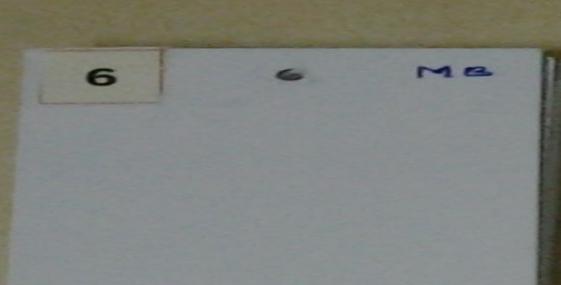


Fig. 59 MS Panels kept in (A) *Arthrospira platensis*; (B) *Chlorococcum humicola*; (C) *Amphora coffeaeformis*. L: Nano-treated panels, R: Control panels

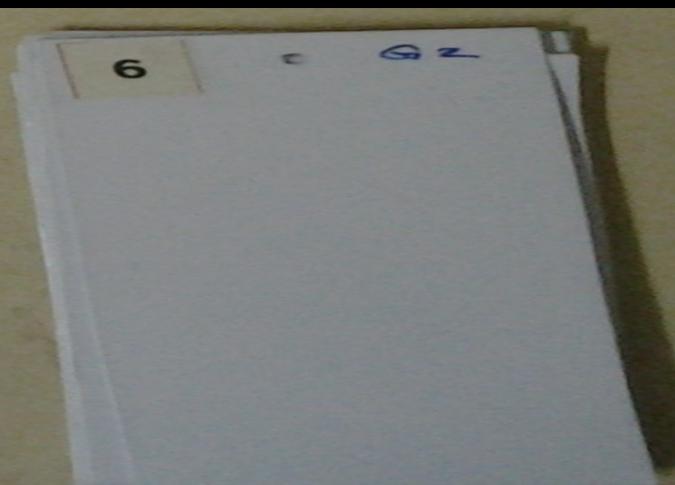
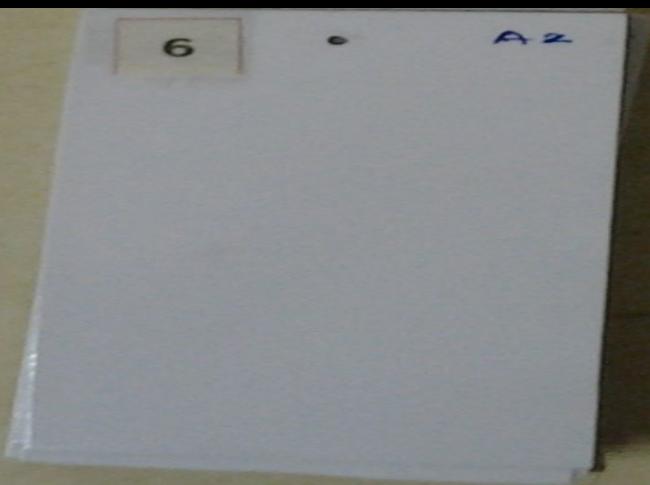
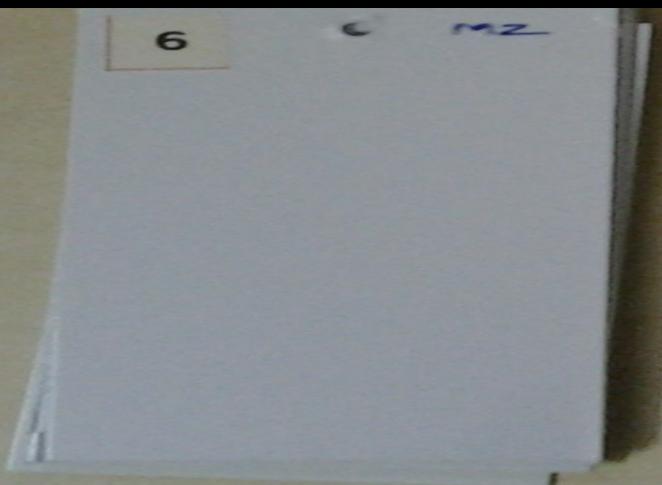
Anti-biofilm Studies with Bacteria

- Yeast and Malt Extract with Glucose (YMG) broth medium (pH 7)
- The treated and untreated GI and MS Panels immersed separately.
- Tubes - sealed and sterilized in an autoclave for 15 mins at 121° C / 15 min. at 15 pounds pressure.
- Cooled in a laminar air flow chamber
- **Pseudomonas spp bacteria** inoculated.





3. Results & Discussion



NZ Coating Process

- Preparation of PNZ conversion bath
- Mixing 1 g to 2 g 50% polyacrylic acid with 500 mL DM water
- Slow addition of 1 to 2 g PNZ powder at RT
- The mixture was made up to 1000 mL by adding DM water
- Neutralizer solution (15%) - 150 g NH_4HCO_3 + 850 g DM water
- The neutralizer solution - for adjusting the pH of the PNZ coating bath.

Bath parameters of PNZ coating process

S No	Stages	Materials required	Temp. (° C)	Time (s)
1.	Sanding	Emery paper (400 – 600 grit)	RT	-
2.	Cleaning	Cleaning thinner	RT	-
3.	Drying	Hot air oven	110-120	60
4.	DM water rinse	Distilled water	RT	60
5.	PNZ Bath	PNZ powder solution 3.0 – 5.0 % w/v at pH 3.5 – 4.5	RT	30-60
6.	DM water rinse	Distilled Water	RT	60
7.	Drying	Hot air oven	110-120	60

*RT = Room Temperature; Temp. = Temperature; Conc. = Concentration; * Neutralizer based on ammonium carbonate added to control pH in the required range.*

Zinc phosphate coating process

Table-1
Bath parameters of zinc phosphating process

S.No.	Stages	Chemicals	% Conc.	T(°C) / t (min)	Remarks
1.	Degreasing	Starclean-430	4-5	60-70 / 5	1) Continuous circulation 2) Floating oils frequently removed on the top of the surface
2.	Water Rinse	Water	-	RT / 10	Continuous Overflow
3.	Derusting	Starpick-440 S	30	RT / 5	Max Iron Content =5%
4.	Water Rinse	Water	-	RT / 1	Continuous Overflow
5.	Water Rinse	Water	-	RT/1	Continuous Overflow
6.	Pre-conditioner	Starfine- FD	0.1 0.2	- RT/1	Continuous air circulation. Age of bath: 1 week max.
7.	Zinc phosphating	Starphos - 531	3.5	65/5	

Contd..

8.	Water Rinse	Distilled water	-	RT/1	Continuous Overflow
9.	Water Rinse	Distilled water	-	RT/1	Continuous Overflow
10.	Passivation	Starpas – 6	0.05	70/1	Age of bath: 1 week max.
11.	Drying	-	-	110- 120/10	-

RT = Room Temperature; Conc. = Concentration

ZnP vs NZ – Visual Examination

Zinc phos

Zinc Phosphate Coating

- Slightly thick
- Opaque
- Colour: light grey
- Crystalline
- Soft matt and forms nail marks



NZ

NZ Coating

- Very thin
- Transparent
- Colour on MS – like pale gold lacquer
- Hard and smooth
- Leaves no nail marks



XRD Studies

ZnP

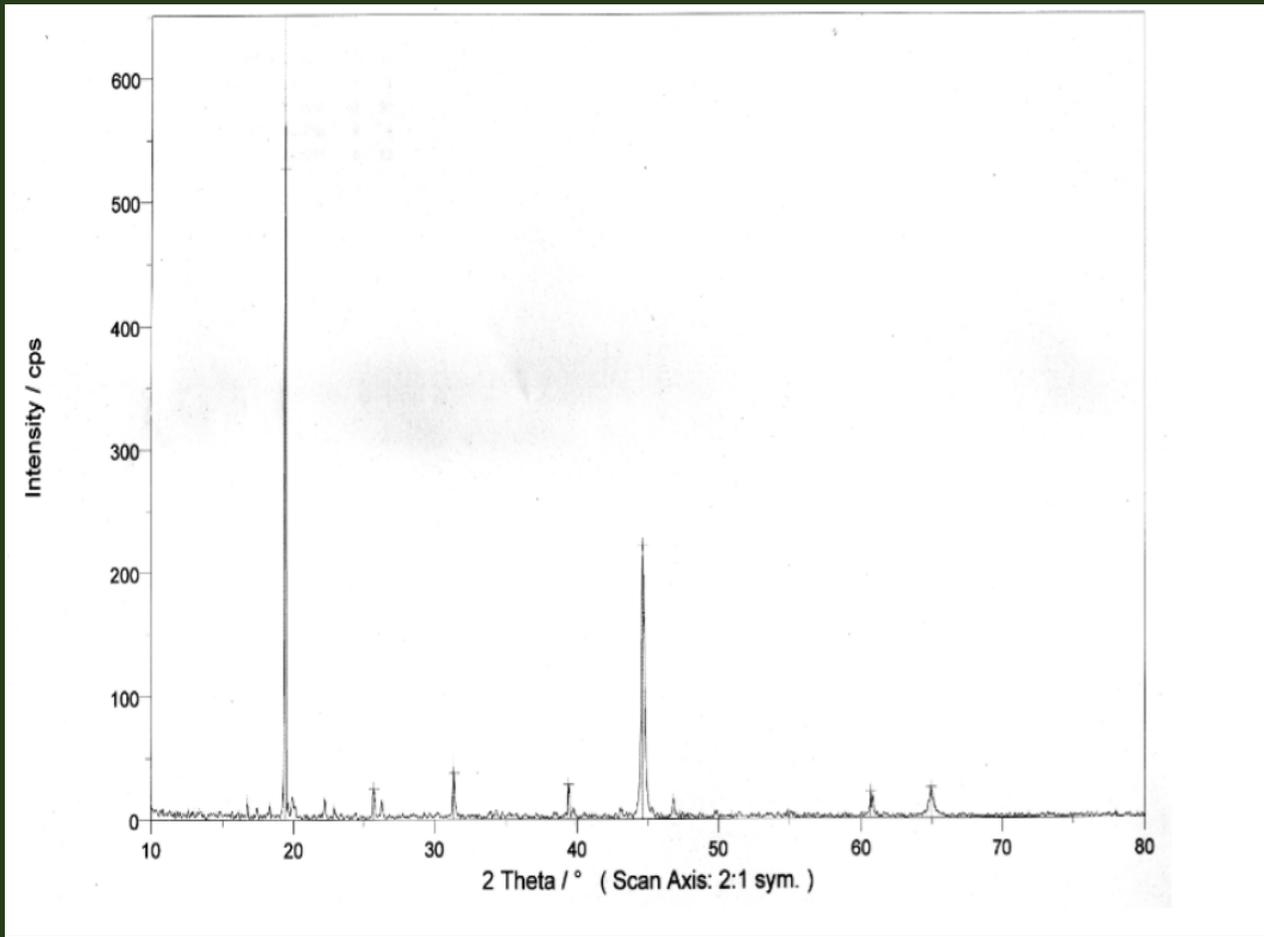
- The sharp peaks at 2θ values 44.55, 19.8 and 32.8
- Fe 110, hopeite $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ and phosphophyllite $\text{Zn}_2\text{Fe}(\text{PO}_4)_2$
- The high intensity of hopeite peak - the dominant coating by hopeite
- The primary coating - needle like network of phosphophyllite crystals
- Top coat with hopeite.

NZ

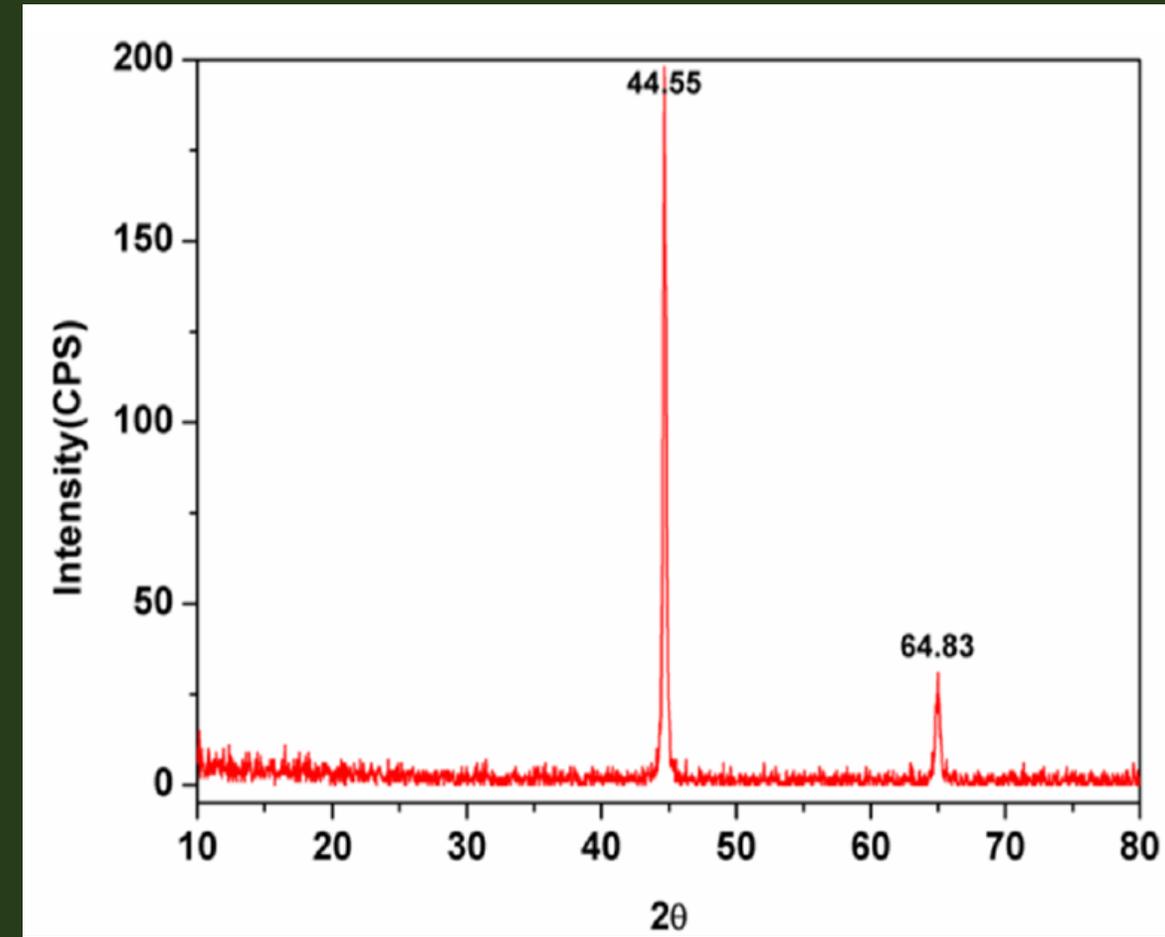
- The sharp peaks at 2θ values 44.55 and 64.83 - Fe 110 and 200 respectively.
- The absence of Zr peak – no clue regarding the type of crystalline structure.
- May be due to the lowest relative composition
- Indicates the thinnest amorphous NZ film on the metal.

XRD Spectra

ZnP



NZ



XRD Analysis

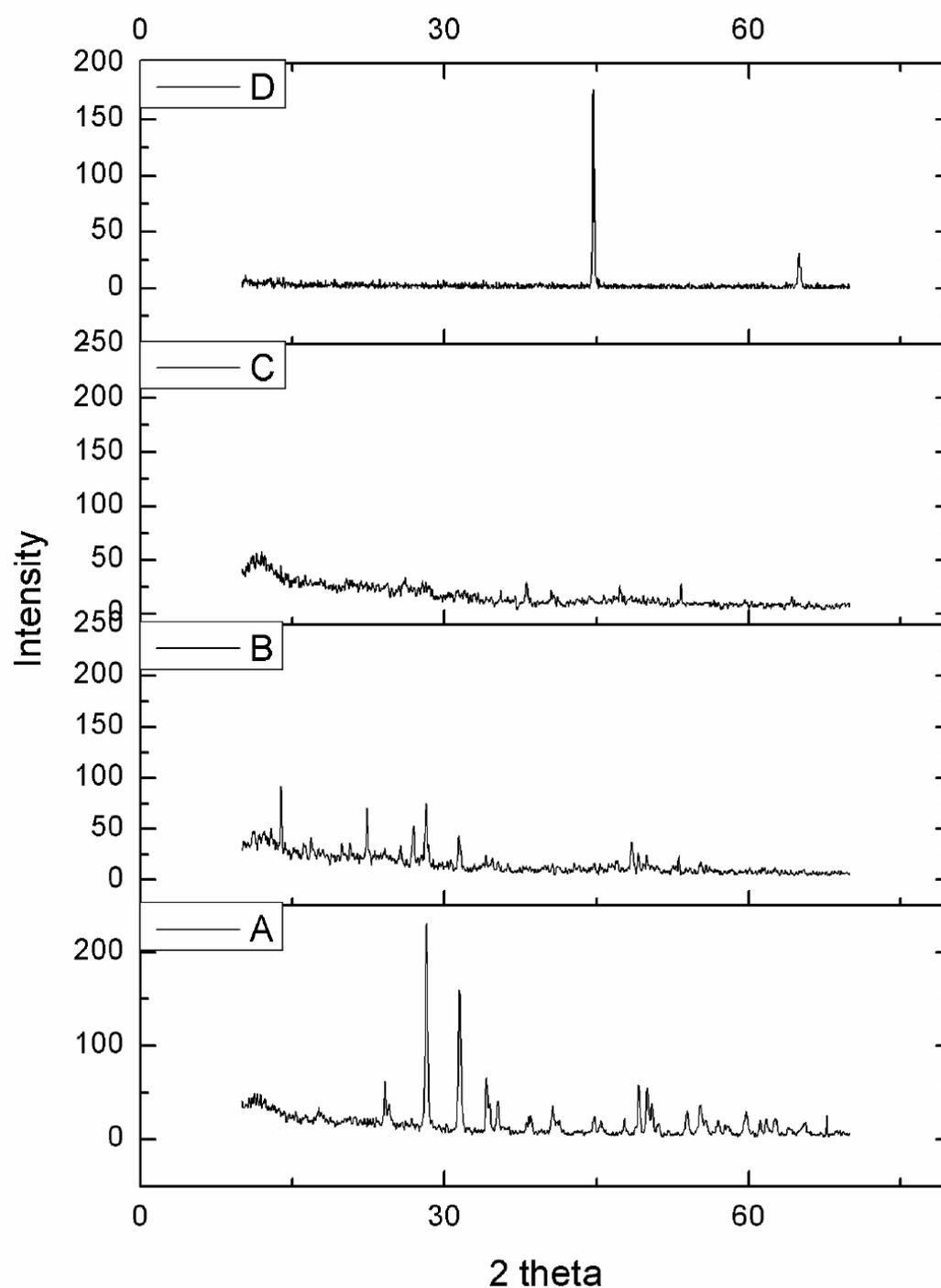
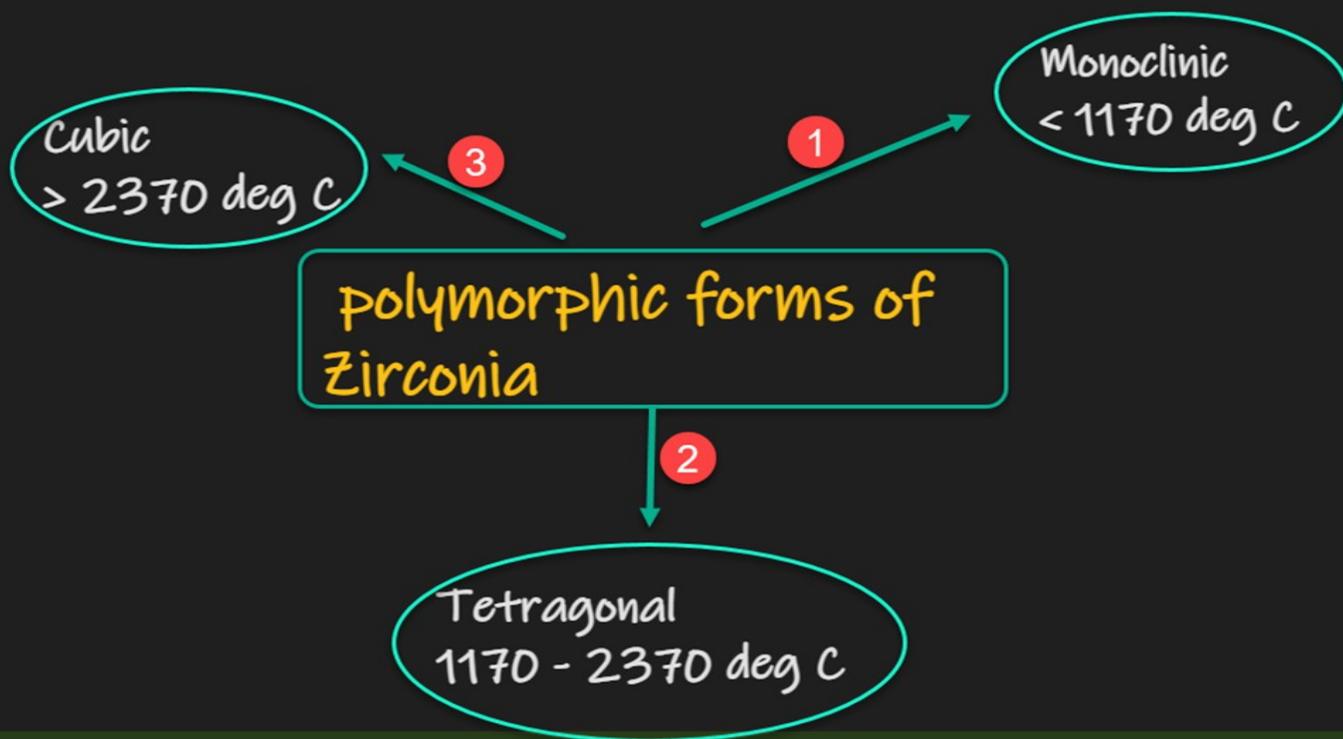
XRD Spectra of PNZ coated and uncoated MS

A – Zirconia powder

B - H_2ZrF_6 powder

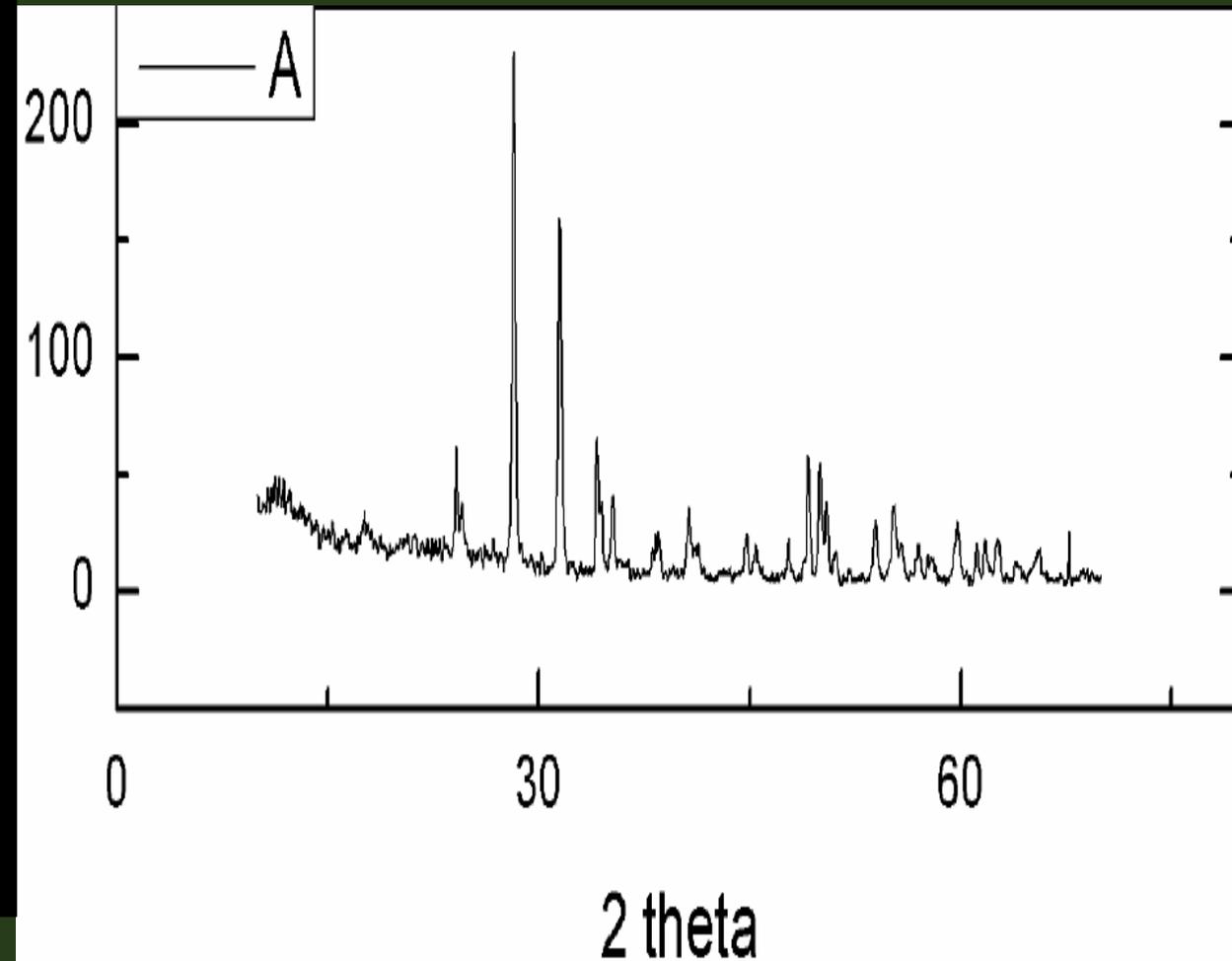
C - Insoluble white residue

D - PNZ coated MS



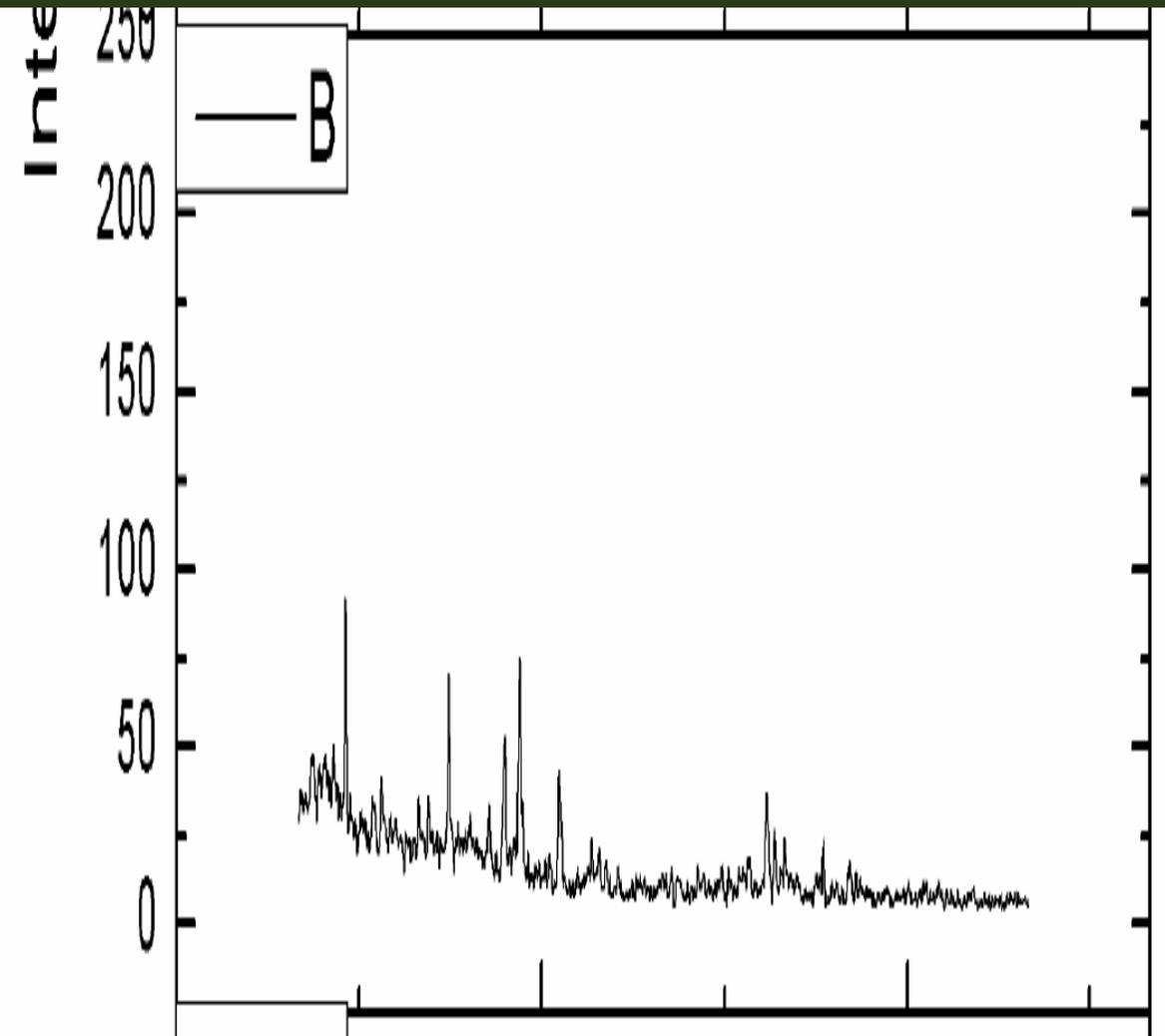
A) XRD Pattern of Zirconia Powder

- Monoclinic phase - the peaks at 2θ values 28.2, 31.5, and 50.1
- Match with the standard values for zirconia (Joint Committee on Powder Diffraction Standards (JCPDS) File no. 371484).
- Trace of Tetragonal phase - The weak peaks at 2θ values 30.2, 50.2, and 60.2 - JCPDS File no. 791769.
- Peak intensity values indicate the **dominance of monoclinic phase** is dominant over the tetragonal phase in zirconia.



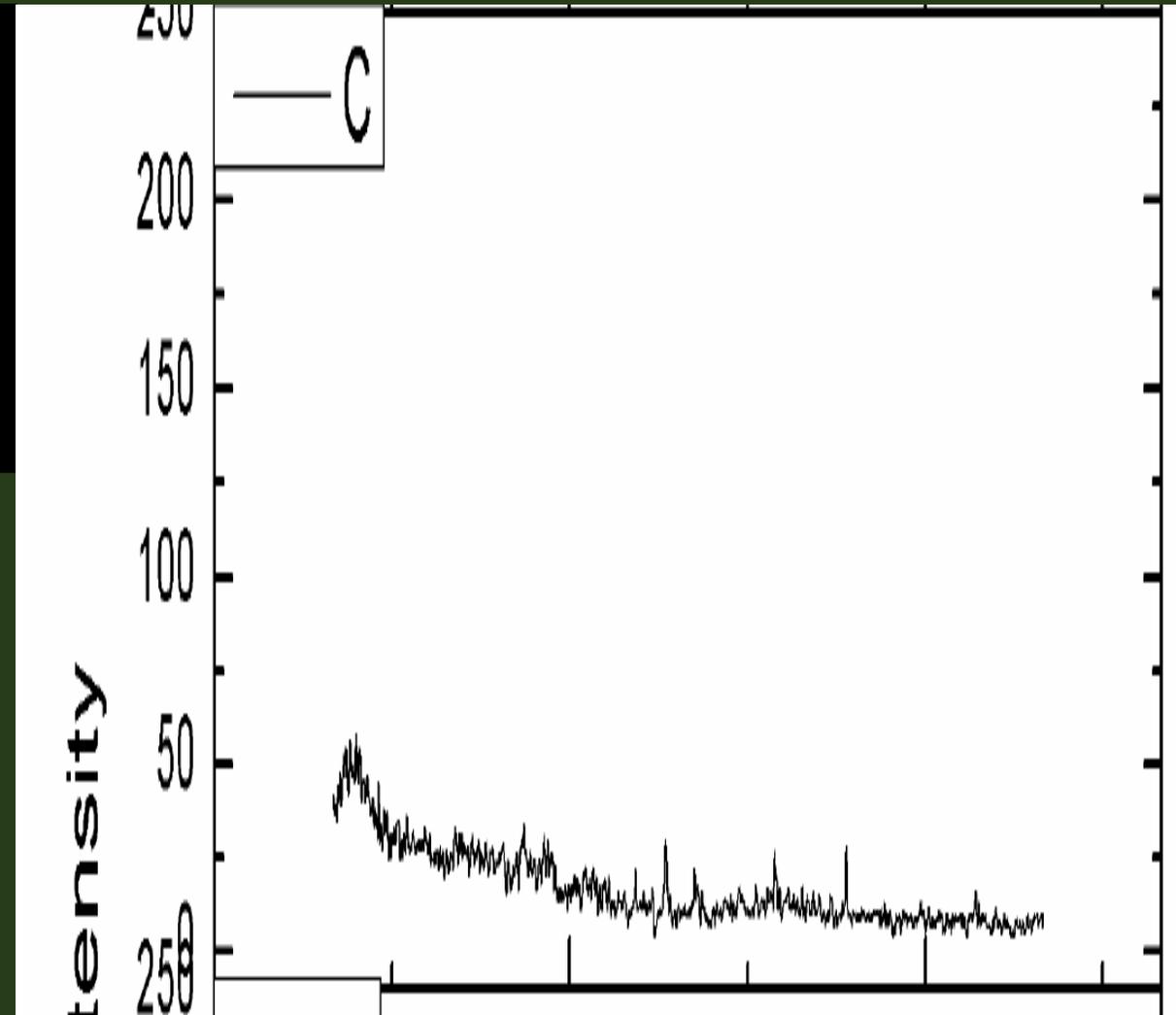
B) XRD Pattern of H_2ZrF_6 Powder

- The diffraction peaks of **monoclinic** phase noticed in zirconia are **absent** in the XRD pattern of H_2ZrF_6 powder.
- The peak multiplicity indicates the increasing tendency to **tetragonal phase** in H_2ZrF_6 powder.
- The major peak observed at 2θ value 15 represents the fluoride ion and the corresponding value is in agreement with JCPDS data for fluoride ions.



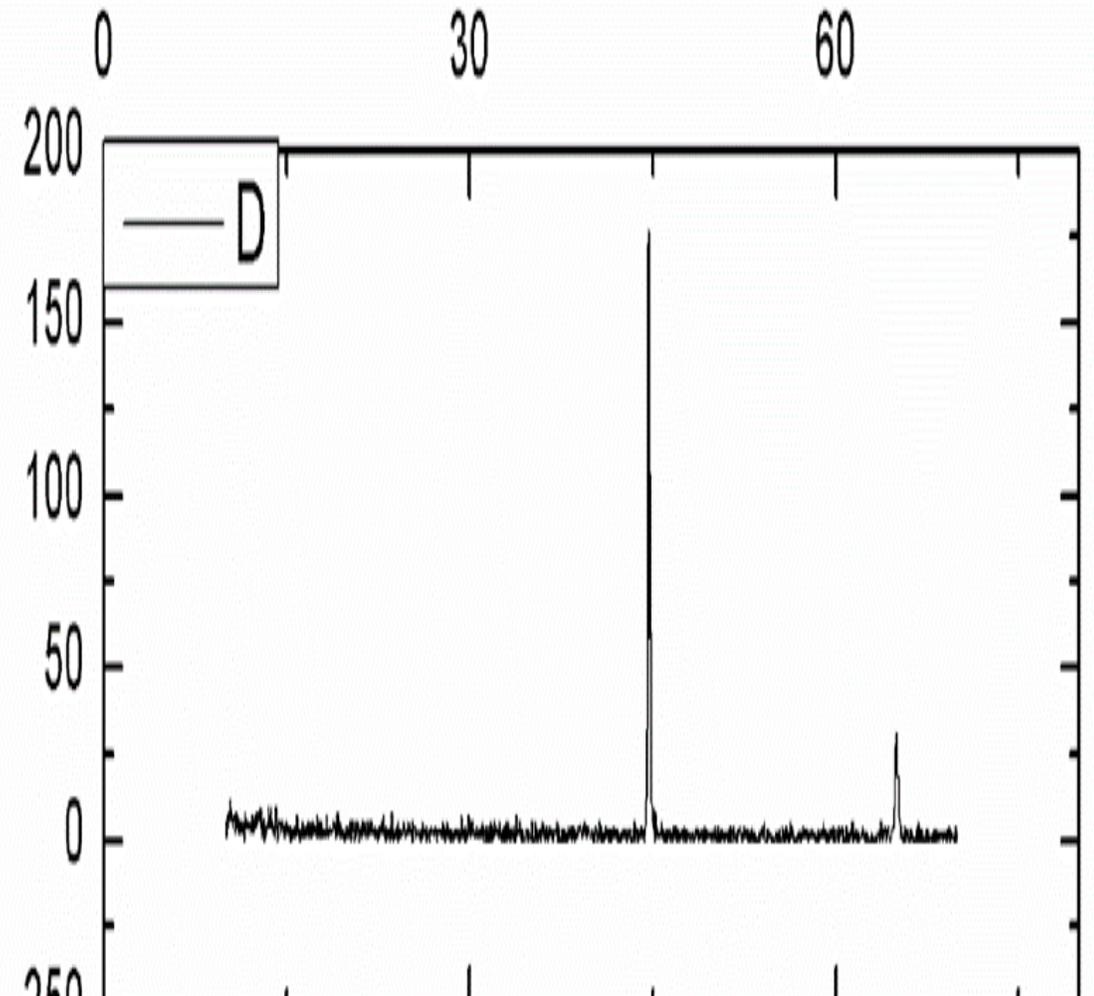
C) XRD Pattern of Insoluble White Residue

- The crystalline zirconia peaks are not traceable in the insoluble white residue
- indicating the complete conversion of zirconia into zirconic acid
- leaving the least amount of zirconia in the insoluble white residue.



D) XRD Pattern of PNZ Coated MS

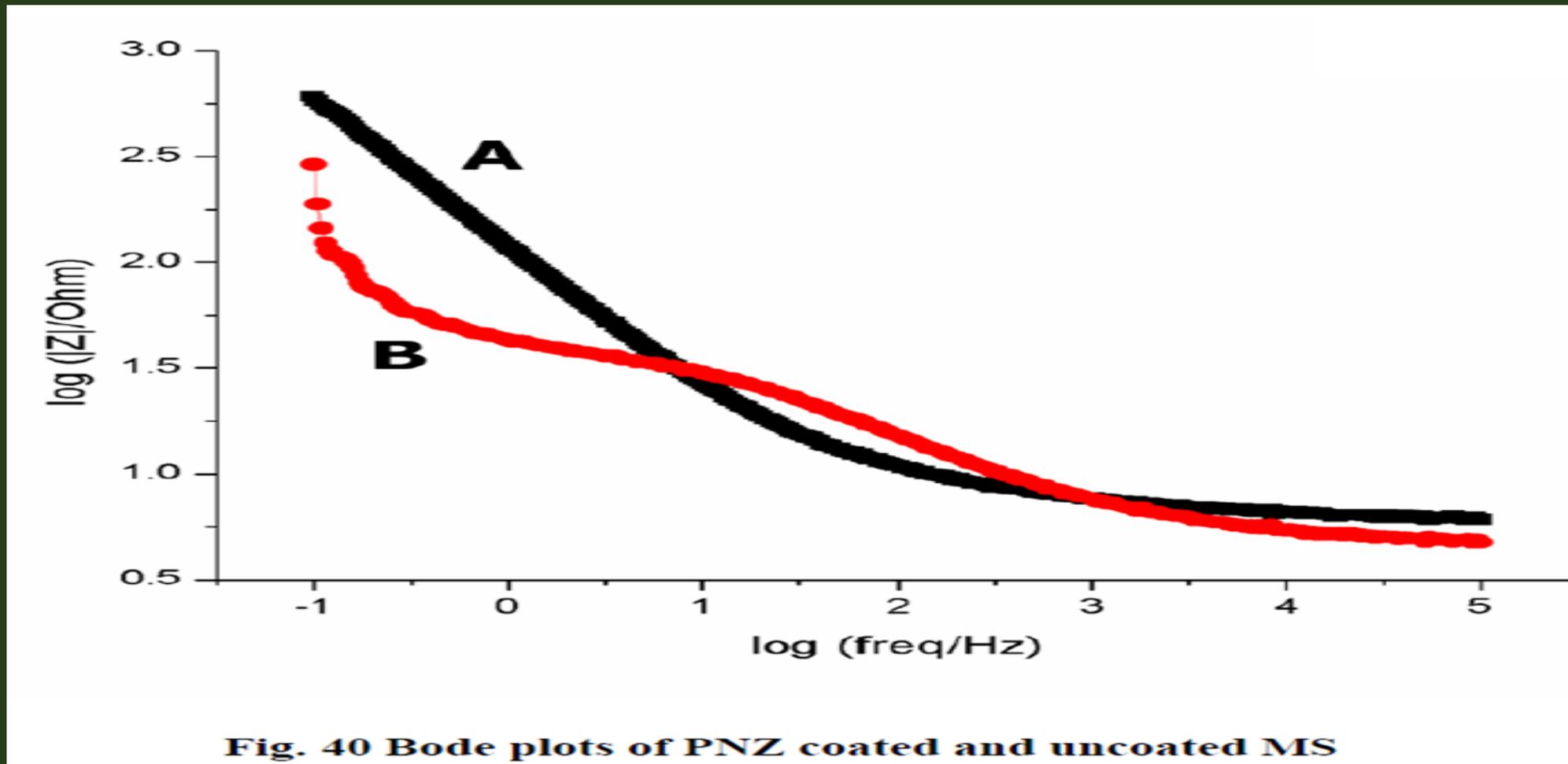
- The X-ray diffraction profile of the top surface of PNZ coated mild steel shows sharp peaks at 2θ values 44.654 and 65.0096
- represent Fe 110 and 200 respectively.
- The absence of Zr peak does not give any clue regarding the type of crystalline structure.
- May be attributed to the lowest relative composition of Zr in the PNZ film or the **amorphous nature** of the coating on the metal.



Electrochemical Impedance Spectroscopy

Bode Plots

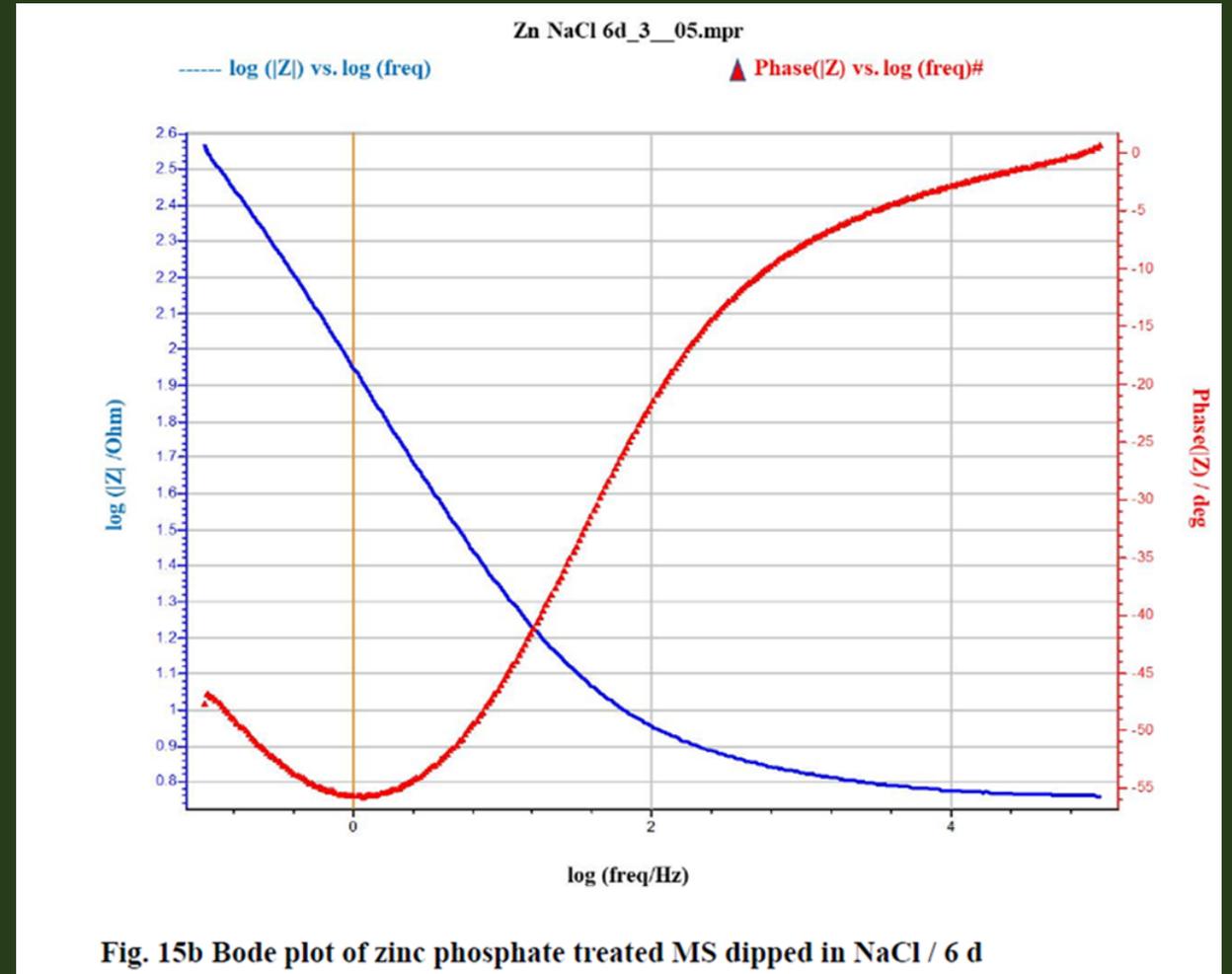
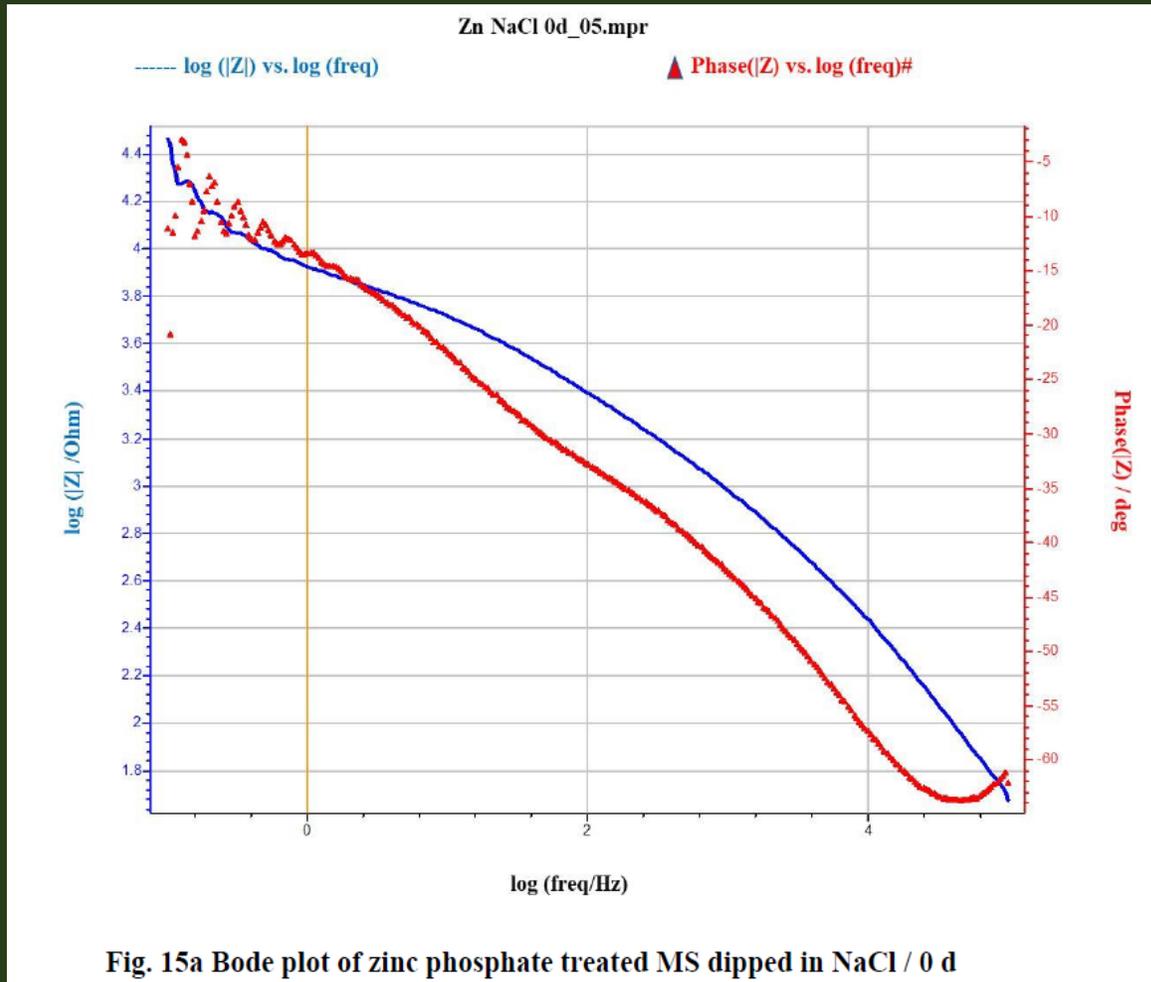
NZ



Electrochemical Impedance Spectroscopy

Bode Plots

ZnP



ZnP

- Bode plots for freshly immersed and 6 d old in 3.5% NaCl solution at open circuit potential
- Slow diffusion of the electrolyte through the pores ZnP coating to the metal.
- A considerable drop in the pore resistance in lower frequency between the fresh and the 6 d old panel kept in the corrosive species.

NZ

- The log $|Z|$ values of Bode plot for UT (B) and NZ (A) were 2.5 ohms and 3 ohms respectively.
- Higher the value for log $|Z|$ better the corrosion resistance of NZ coating on the metal.
- May be the marginal increase in the value.
- Hence, NZ coating needs to be overcoated immediately with top coat

Nyquist Plots

ZnP

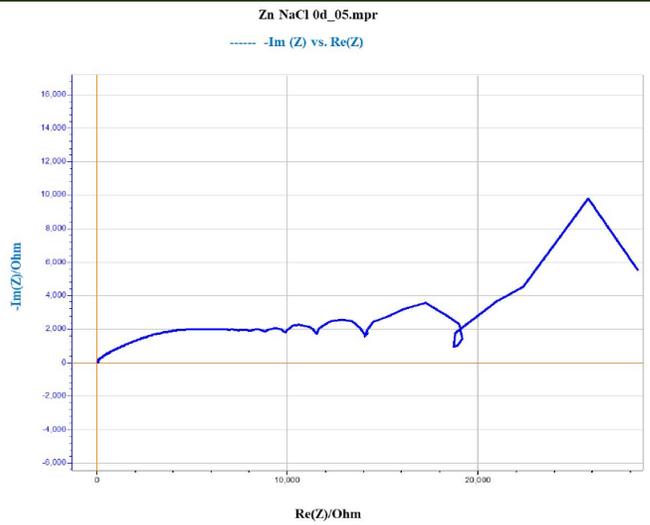


Fig. 16a Nyquist plot of zinc phosphate treated MS dipped in NaCl / 0 d

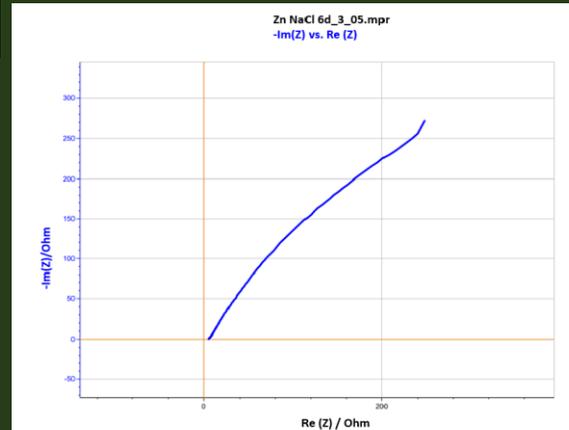
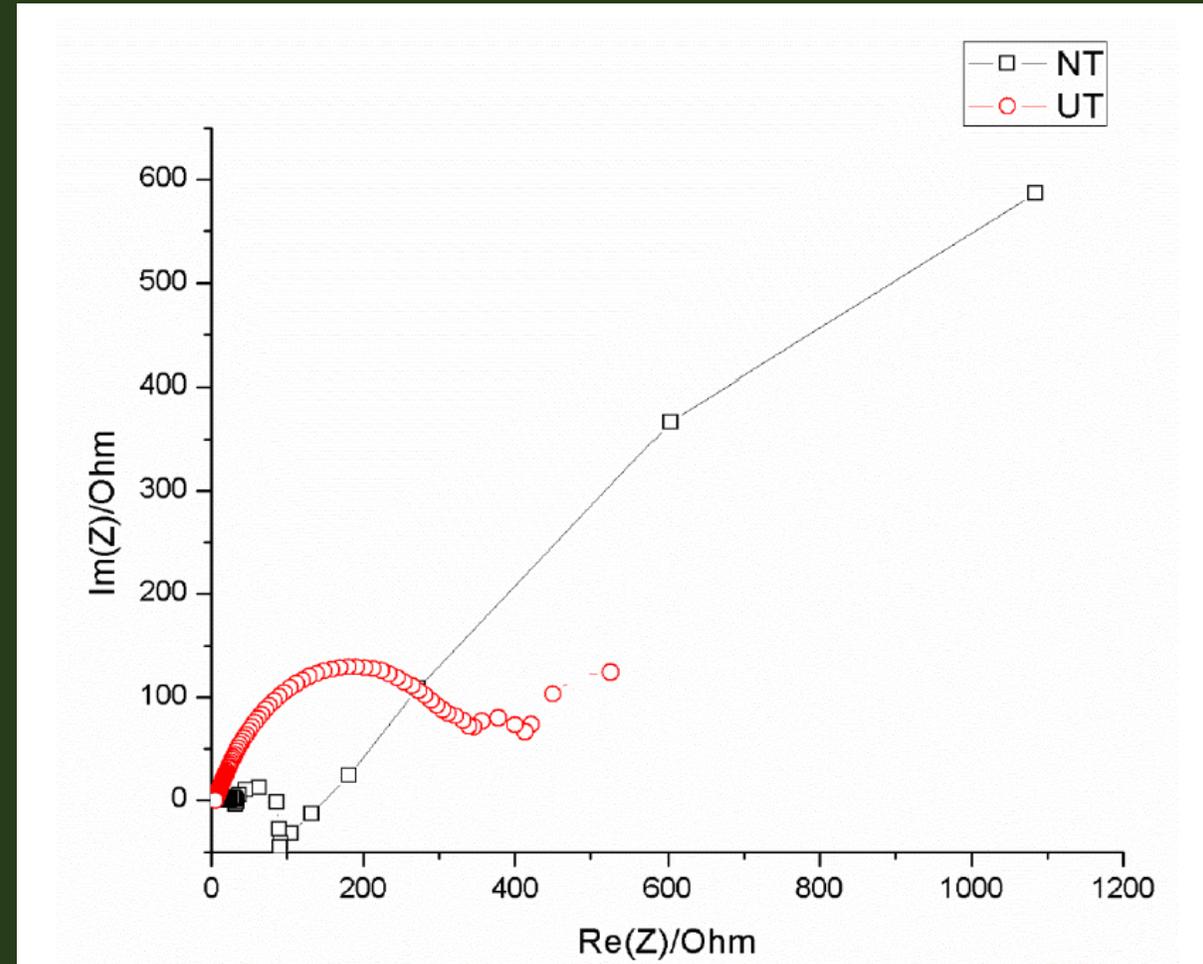


Fig. 16b Nyquist plot of zinc phosphate treated MS dipped in NaCl / 6 d

NZ



Nyquist Plots

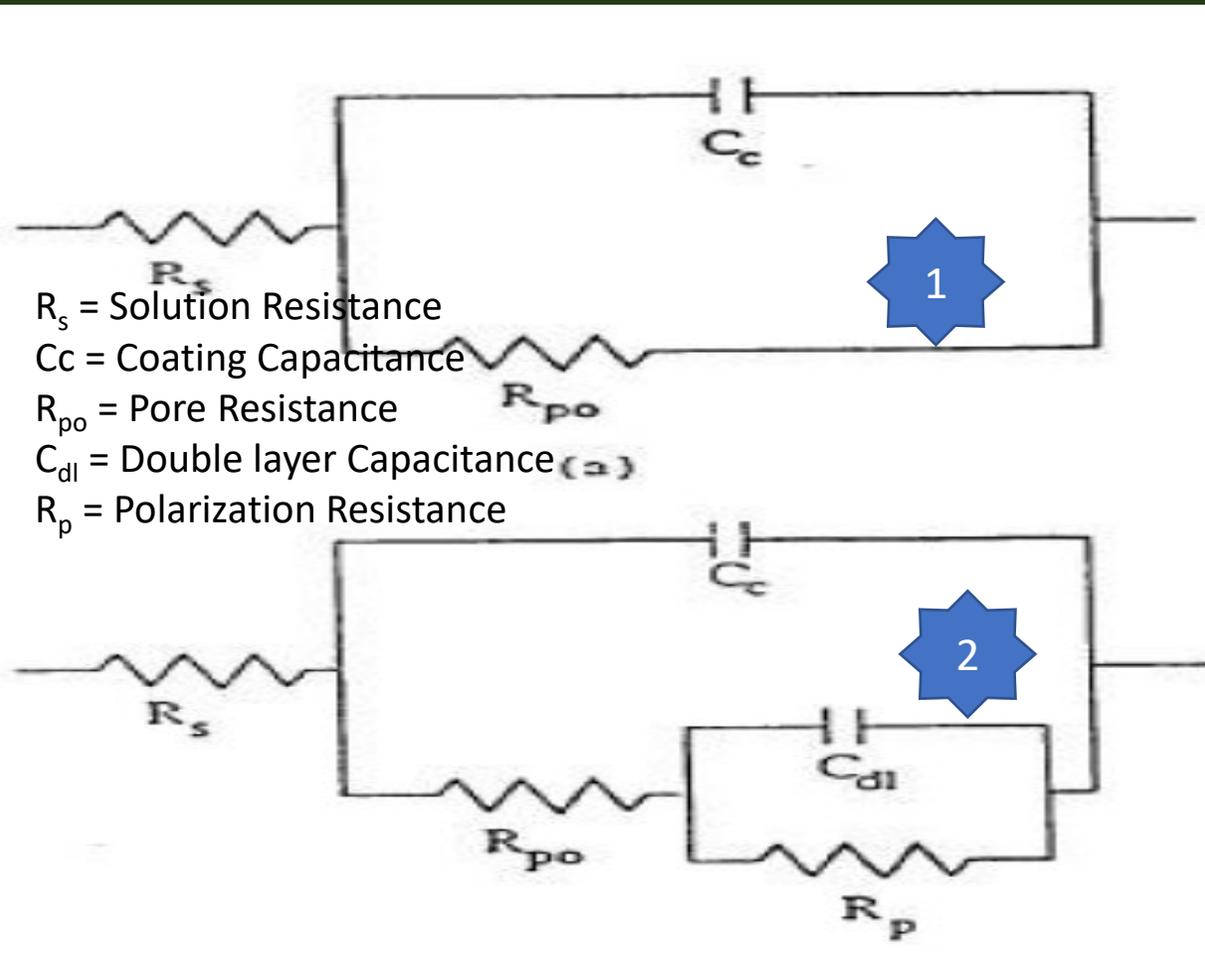
ZnP

- ZnP- an **insulated inorganic coating**
- Not directly involved in electrochemical reaction.
- **Corrosive ion enters the metal surface** through the **pores of phosphate layer**.
- The phosphate coating by itself - not corrosion resistant
- has **micropores** that facilitates the **diffusion of corrosive species**.
- In 6 d old panel, the **pore resistance** further **dropped** - the phosphate film is considerably affected by the corrosive species.
- But, no pores – no adhesion of top coat – missing of anchoring points.

NZ

- **Untreated MS** - the characteristic **semicircle** - indicating a time constant [Basiruddin et al].
- The **characteristic semicircle was suppressed in the Nyquist plot**.
- The present coating system did not represent a true capacitor.
- The thin **NZ coated MS panels sensitive to moisture**.
- Prolonged exposure without top coat paint results in **flash off spot rust**.
- Increase in the charge transfer resistance of NZ coating over uncoated MS

Equivalent circuit of the electrochemical reaction



First Circuit

- Represents the coating without damage
- Pore resistor and coating capacitor in parallel
- Initially high coating resistance (R_{po})
- Developed at lower frequency
- Due to the capillary pores of zinc phosphate coating
- Coating capacitance (C) inversely proportional to pore resistance (R_{po}) or impedance at lower frequency (f).

The second circuit

- Indicates the damaged coating
- Polarization resistor (R_p) and double layer capacitor (C_{dl}) connected in parallel
- At higher frequencies the coating - attack of the corrosive species leading to polarization resistance (R_p).
- Later, an electric double layer is established

Linear Polarization Studies

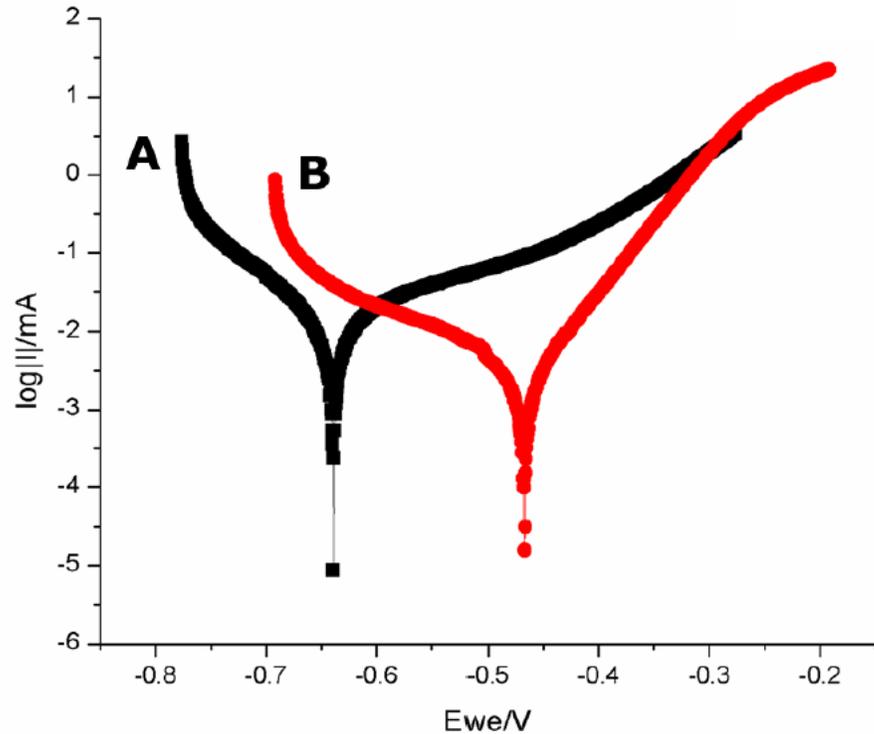


Fig. 38 Tafel plots of PNZ coated and uncoated MS

(A) PNZ on MS, (B) Uncoated MS

- The corrosion rates of NZ treated and untreated MS panels without top coat paint were calculated from Tafel plot
- The polarization resistance (R_p) for the NZ treated MS (8.77 $k\Omega$) higher than that of the untreated one (6.34 $k\Omega$)
- The higher R_p value of NZ treated MS indicates the better corrosion resistance [Gu et al] than that of the untreated MS.

Linear Polarization Studies

- The corrosion rates of PNZ and NT coatings are 1.13 and 1.10 mpy respectively
- Both these values are less than that of untreated MS (1.32 mpy).
- Corrosion rate in terms of mpy for a well protected mild steel surface is 3.45
- For steel, mpy = 1.0.
- No much wider difference in the corrosion rate between treated and untreated base metal.
- The **conversion coating by itself is not corrosion preventive**
- **Need for immediate top coat** with paints.

Table-24 Linear polarization parameters for corrosion of treated and untreated MS

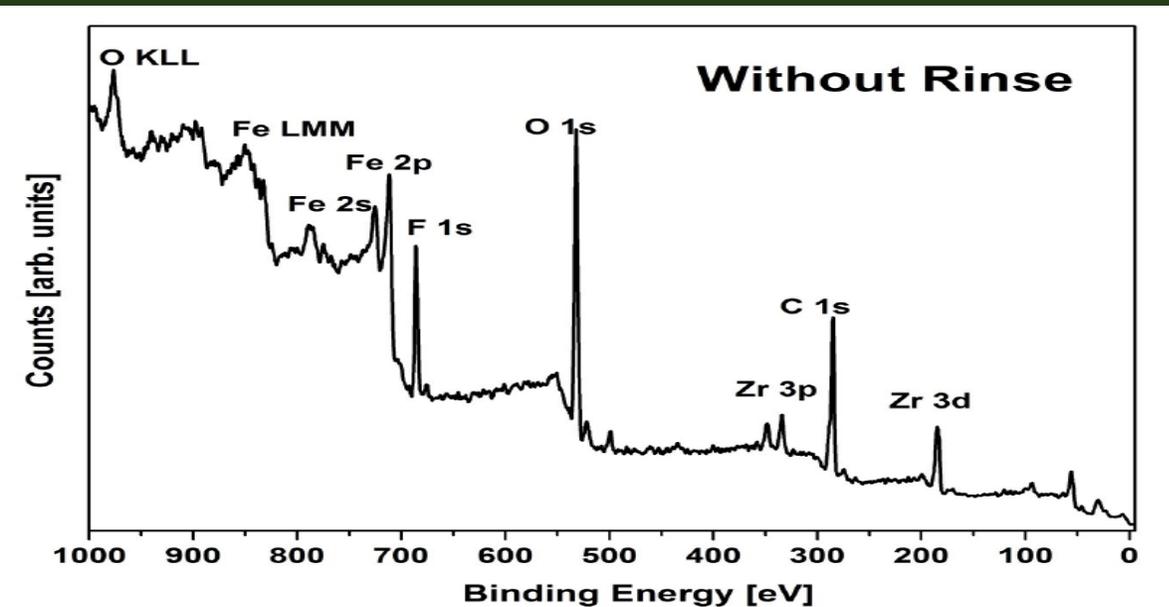
MS Panel	E_{corr} (V/SCE)	I_{corr} (μ A/cm ²)	α (mV/dec)	β (mV/dec)	CR (mpy)	R_p (k Ω)
UT	-0.460	2.86	57.1	156	1.32	6.34
PNZ	-0.640	2.46	73.9	151	1.13	8.77
NT-1*	-0.530	2.34	79.2	90.0	1.10	7.83

MS – Mild Steel, UT – untreated, PNZ – Pure Nanozirconia coated MS

E_{corr} – corrosion potential, I_{corr} – corrosion current, α -Tafel anodic slope, β -Tafel cathodic slope, R_p – polarization resistance.

* Bonderite NT-1

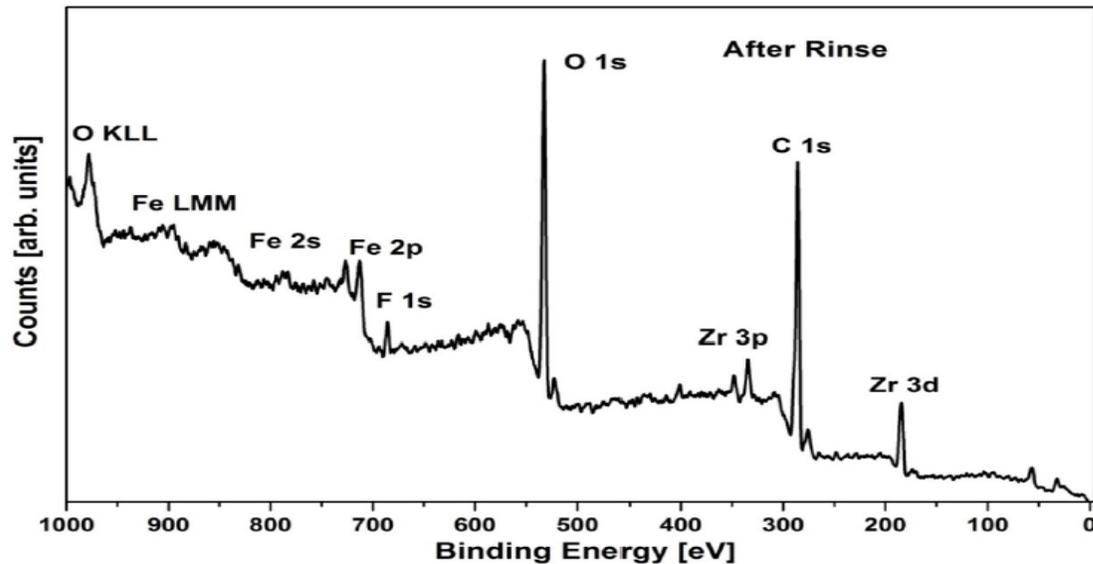
XPS Spectrum of NZ/MS Without Rinse



- The NZ coated mild steel panels without rinse and after rinse - X-ray photoelectron spectrometer (XPS)
- To investigate the presence of oxides and fluorides of Zr and Fe, hydroxyl group and adsorbed water.
- **Without rinse:** Zr 3p, Fe 2p, F 1s, and O 1s peaks at 334 eV, 711 eV, 686 eV and 532 eV
- Atomic composition: Zr = 1.6%
- The F composition = 7.6%

Name	Position	FWHM	% At Conc.
O 1s	532	3.7	29.5
C 1s	285	3.1	56.1
F 1s	686	3.3	7.6
Fe 2p	711	5.1	5.2
Zr 3p	334	3.8	1.6

XPS Spectrum of NZ/MS After Rinse



- **After rinse:** Zr 3p, Fe 2p, F 1s, and O 1s peaks at 334 eV, 713 eV, 686 eV 532.5 eV respectively.
- The atomic composition of Zr 1.4% on the after rinse sample.
- The F composition less in the rinsed sample (1.1%) than in the unrinsed sample (7.6%)
- Indicates major fluorides ions washed off during the post rinse operations with distilled water.
- The composition of the coating contains only Zirconium oxide in hydrated form and not as fluoride.

Name	Position	FWHM	% At Conc.
O 1s	532.5	3.8	23.2
C 1s	285.5	3.5	72.9
F 1s	686	3.6	1.1
Fe 2p	713	5.8	1.5
Zr 3p	334	4.0	1.4

XPS Depth Profile of Rinsed Sample

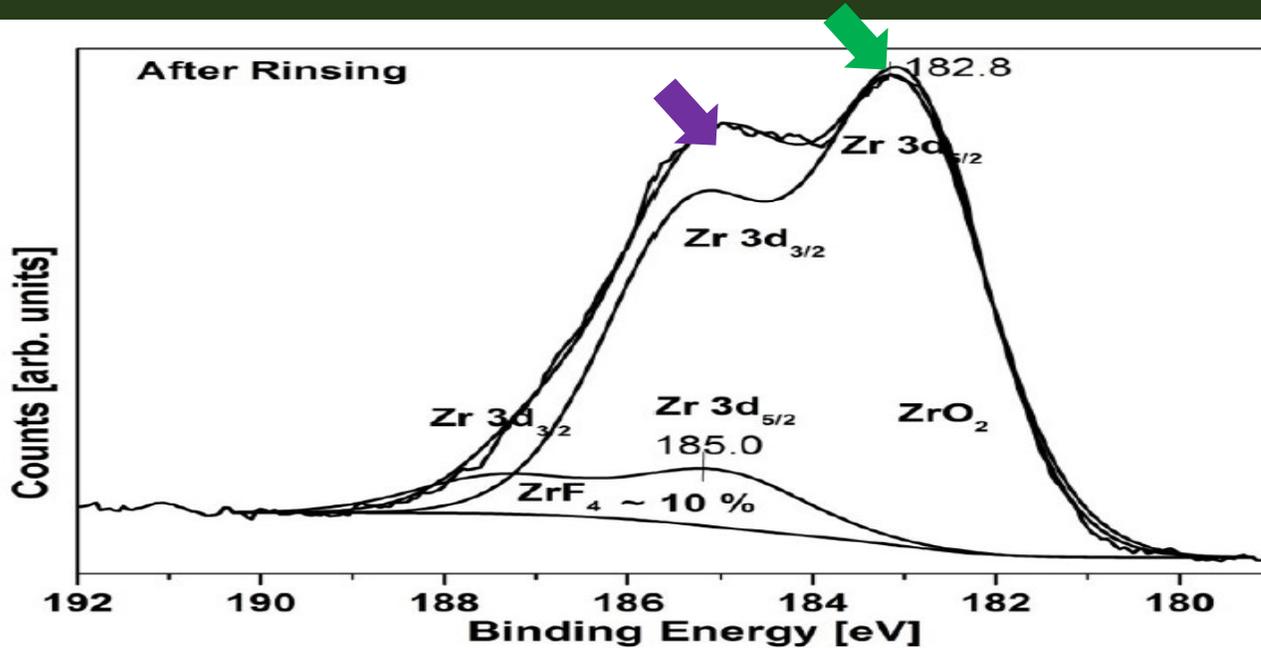


Fig.29e. XPS profile of ZrO₂ and ZrF₄ after rinse

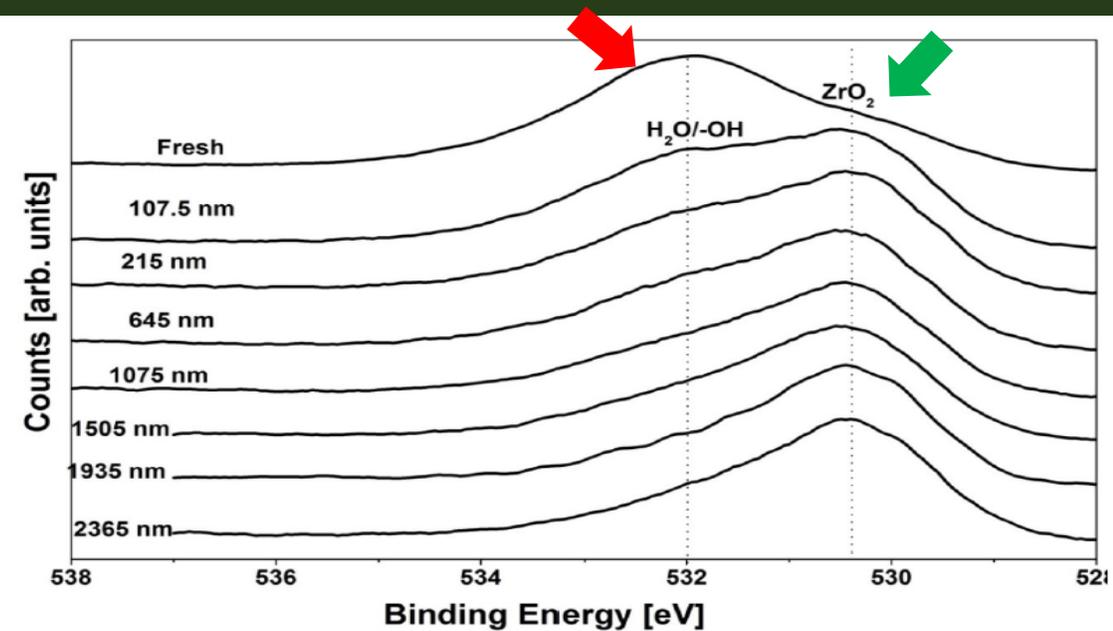


Fig.29c. XPS profile of OH⁻ ion, H₂O and ZrO₂

- Diminishing peaks of H₂O/-OH peak at 532 eV and the predominance of ZrO₂ at 530.5 eV .
- The intensity of the peak of Zr 3d_{5/2} at 182.8 eV (ZrO₂) > in rinsed than in unrinsed.
- The Zr 3d_{3/2} (ZrF₄) peak reduced in rinsed sample - ZrF₄ loosely held & removed.
- Fine coating of ZrO₂ predominant on hydroxyl sites of iron surface.

XPS Depth Profile Unrinsed Sample

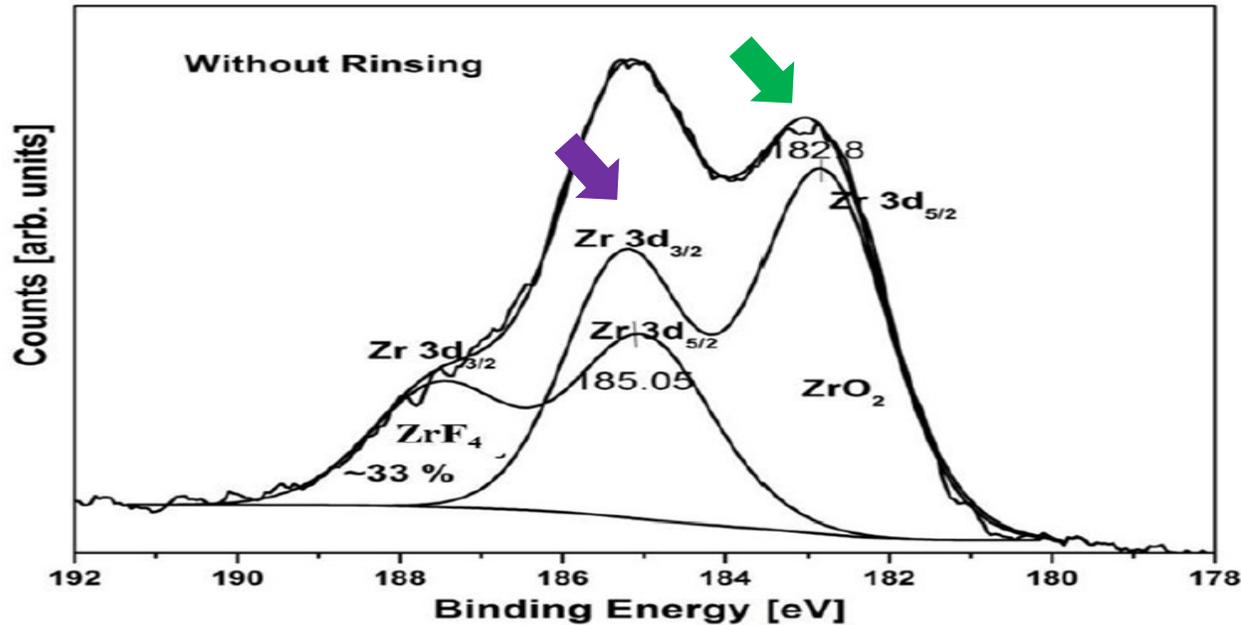


Fig.29d. XPS profile of ZrO₂ and ZrF₄ without rinse

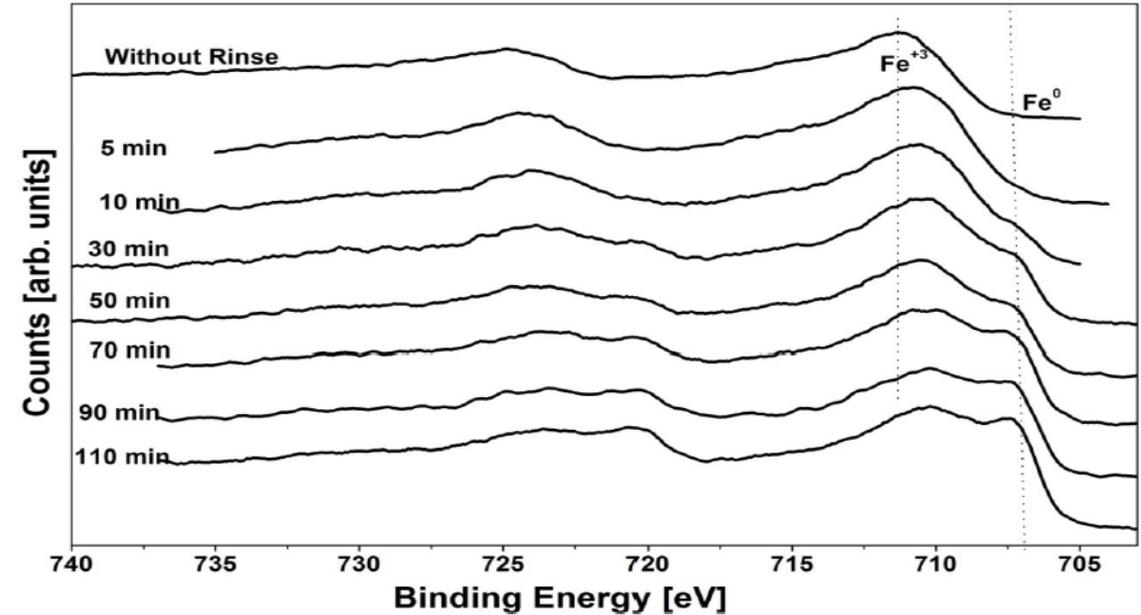
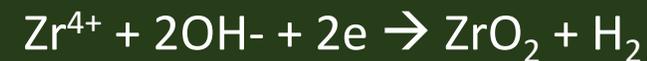
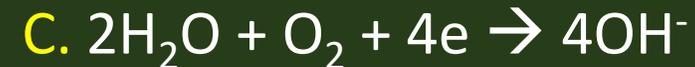


Fig.29f. XPS depth profile of Fe 2p without rinse

- The profile of Zr in the unrinsed sample shows Zr as oxide and fluoride.
- The intensity of the peak of Zr 3d_{5/2} at 182.8 eV (ZrO₂) less in unrinsed.
- The Zr 3d_{3/2} (ZrF₄) peak dominating the ZrO₂ peak

Mechanism of NZ Coating on MS

- A. Initial dissociation of hexafluoro zirconic acid
- B. Oxidation at anodic site. Ref. XPS Fe³⁺ peak at 711 eV
- C. Reduction at cathodic site. Ref. Fe³⁺ peak diminishes on sputtering. Fe⁰ state at >10nm depth – possible layer thickness of zirconia
- D. Electrochemical cell reaction and zirconia coating on hydroxyl sites.
- E. Fine deposition of hydrous nano zirconia on MS



XPS Studies of H_2ZrF_6 and PNZ Coated panel

H_2ZrF_6 powder

Zr 3d_{5/2}, Zr 3p, Zr 3p_{3/2}, Zr 3p_{1/2}, Zr 3s and F1s peaks - at 182.8 eV, 334 eV, 370 eV, 382 eV, 423 eV and 686 eV respectively.

PNZ coated panel

- Zr 3d and Zr 3p - at 182.8 eV and 334 eV respectively.

XPS Spectrum of H_2ZrF_6 Powder

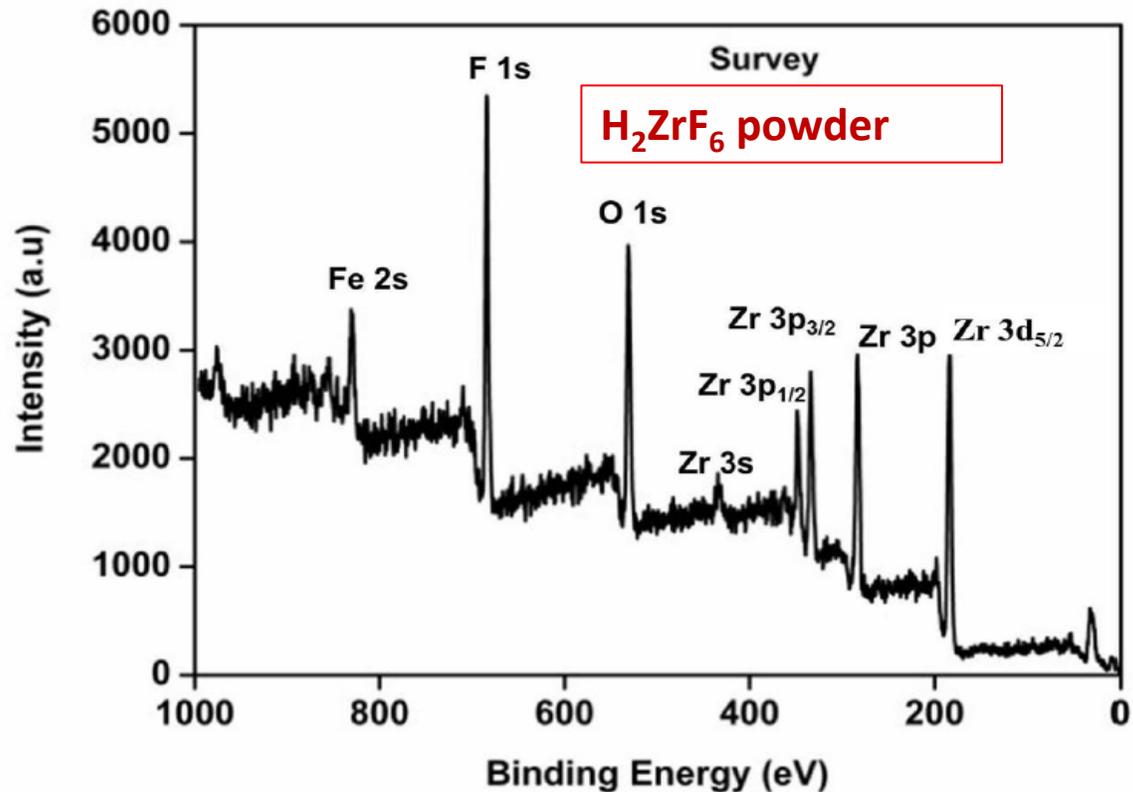
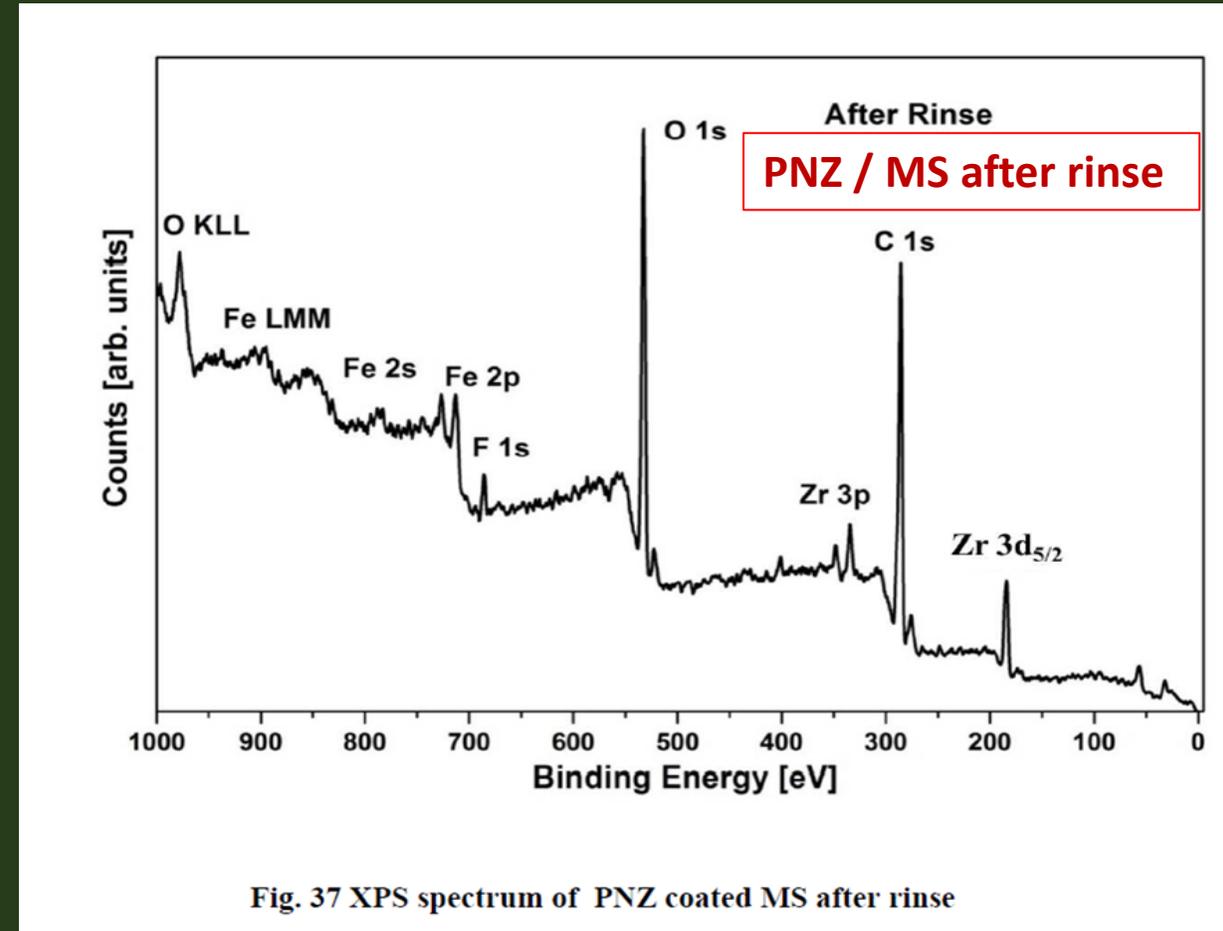


Fig. 36 XPS spectrum of H_2ZrF_6 powder

- The Zr 3d_{3/2} (ZrF₄) peak has considerably lower intensity in the PNZ coated sample than in the H_2ZrF_6 powder.
- Carbon - completely absent in the dry H_2ZrF_6 powder

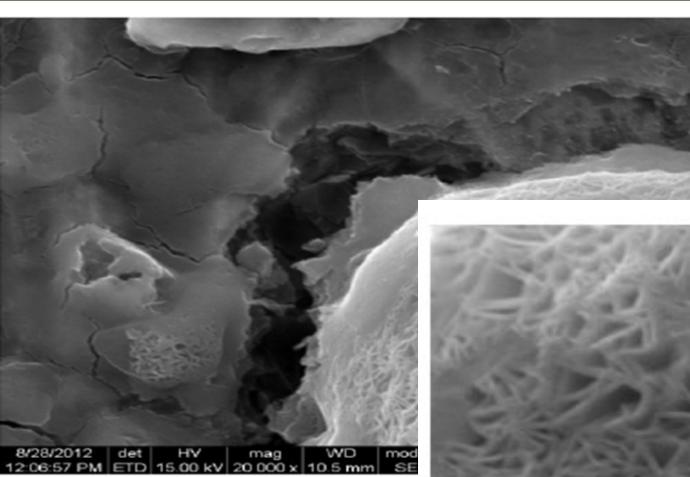
3. XPS Spectrum of PNZ / MS after rinse

- A mild coating of zirconia is obvious from the presence Zr 3d_{3/2} and Zr 3p peaks.
- **Carbon** - present in the PNZ coated sample and may be attributed to polyacrylic acid, the adhesion promoter used in the PNZ bath.
- The intensity of Zr and F peaks are less.
- The **intensity of F peak is weak**
- Most of the **fluoride ions washed off** during the post rinse operations with distilled water.
- A competition for deposition on iron surface between ZrF₄ and ZrO₂.

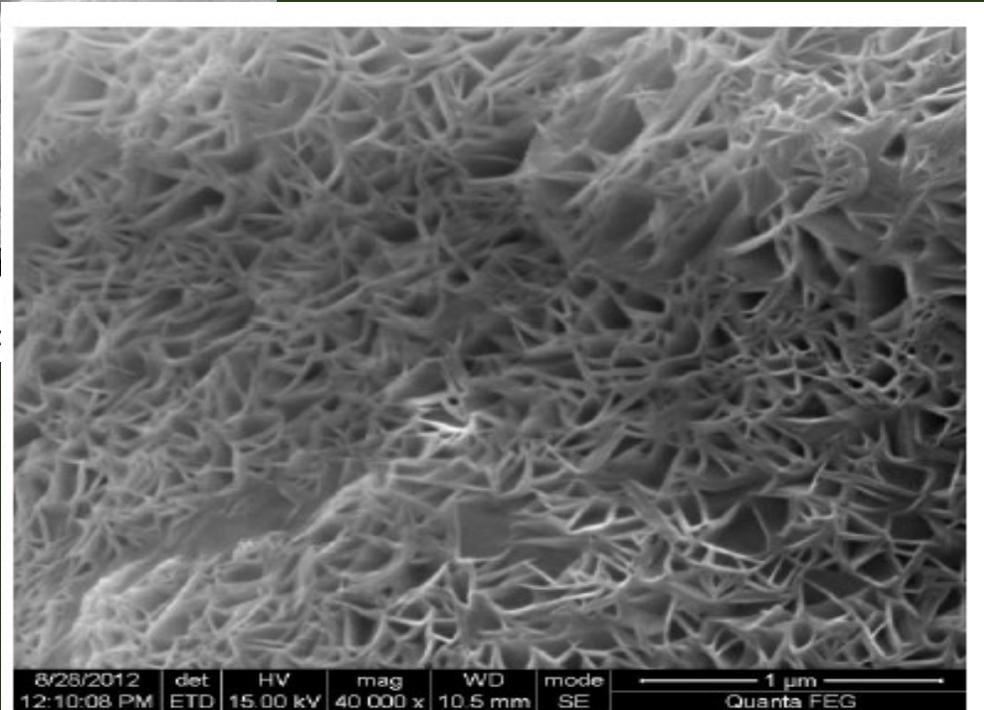


FE SEM

ZnP



(c) 20000 :



(d) 40000 x

NZ

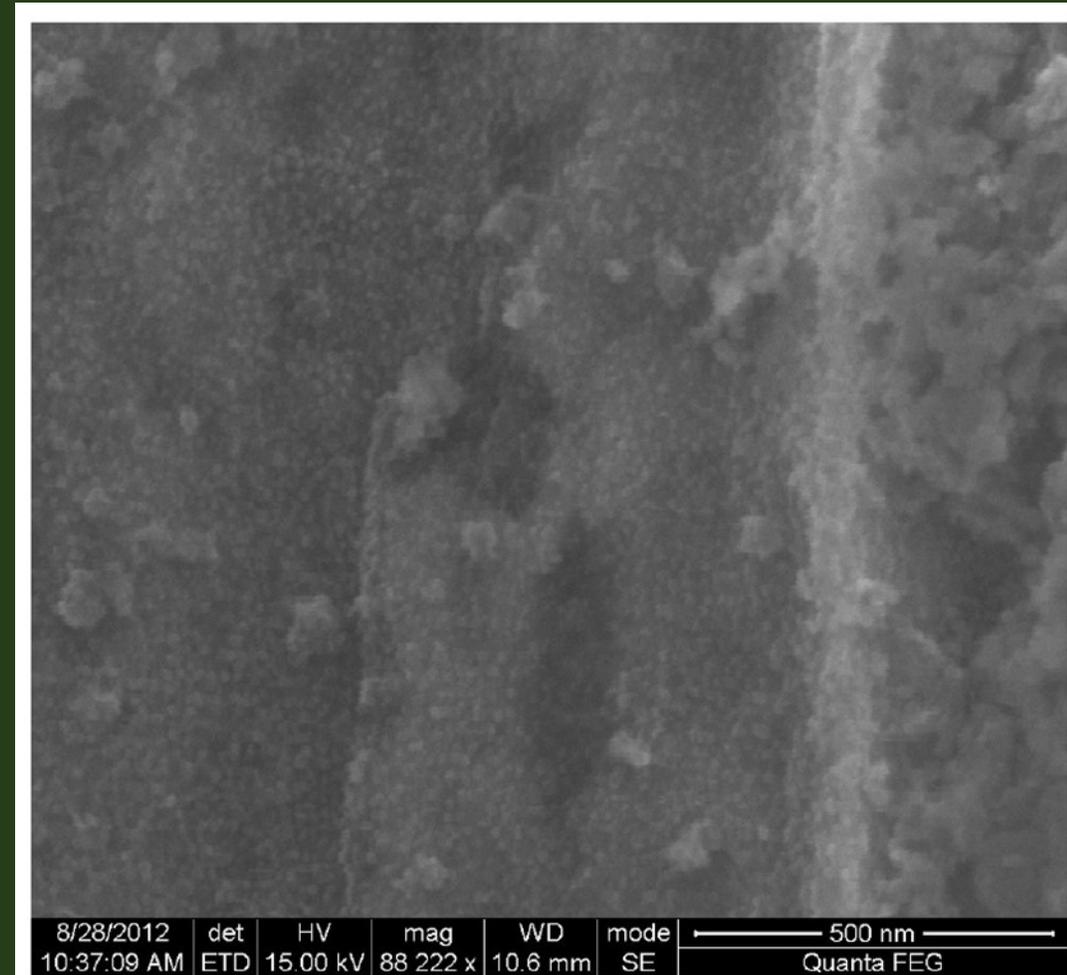
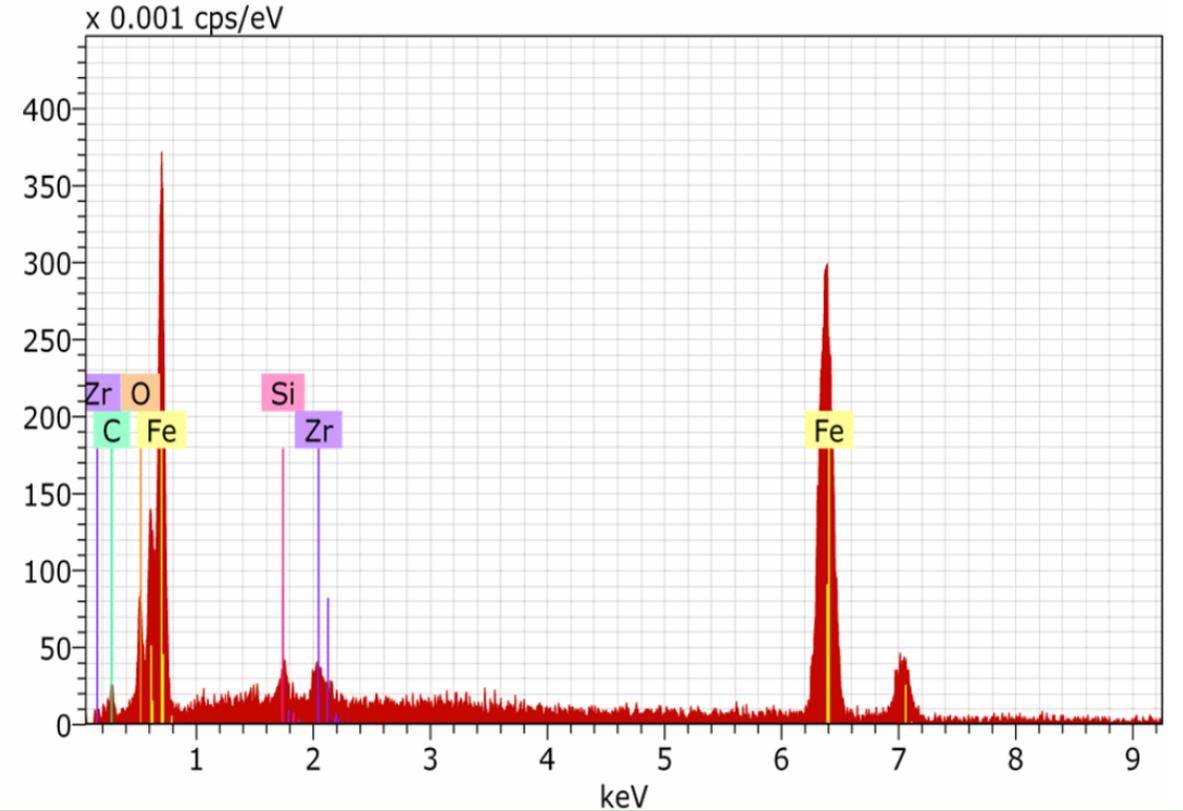
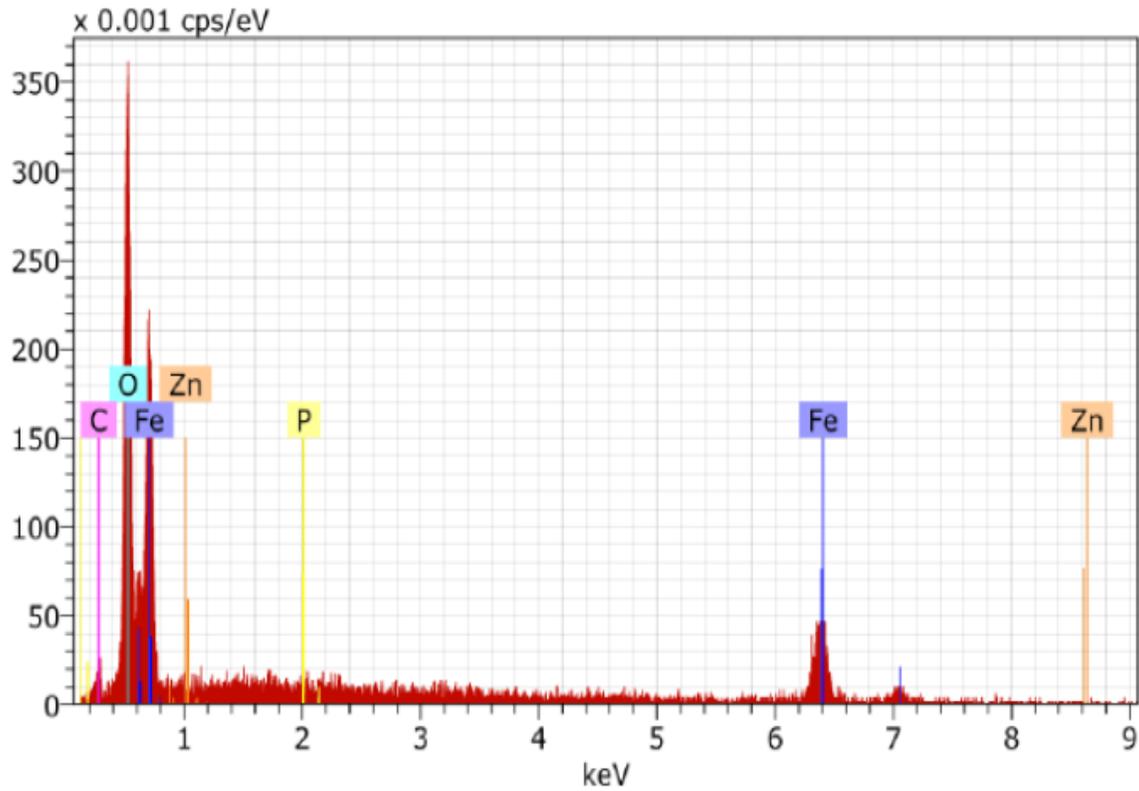


Fig.26 (c) SEM image of NT coating at 88,222 X magnification

EDAX Spectra

ZnP

NZ



FE SEM / EDAX Spectra

ZnP

- A large amount of Fe detected due to the mild steel substrate
- Other peaks of Zn, P, O and a trace of carbon.
- The EDAX peaks at 0.615 keV, 0.705 keV and 6.404 keV, and 7.057 keV represent the Fe(L1), Fe (La1), Fe (Ka1) and Fe (Kb1) respectively.
- The intensities of the peaks at 1 keV and 2 keV - Zn, and P are very weak due to their very low concentration.
- An intense peak of O (Ka1) - observed at 0.525 keV.
- The peaks of Zn, P and O indicate the presence of zinc phosphate film on mild steel.
- The carbon peak may be due to the presence of carbon in the mild steel.

NZ

- Agglomeration of very fine globules at 88222 x magnifications.
- The size of these structures: 20 – 50 nm.
- A large amount of Fe detected in EDAX spectra - mild steel substrate in NZ coating
- Zr Peaks at 0.151 keV and 2.042 keV - Zr (Mz), and Zr (La1) - weak due to very low concentration of Zr.
- F peak at 0.676 keV overlaps with 0.705 keV Fe La1 peak and Fe peak.
- An intense peak of O (Ka1) at 0.525 keV - the oxide film of Zr.
- The carbon peak may be due to the presence of some adhesion promoter.

Powder form of H_2ZrF_6

FESEM and EDAX Studies

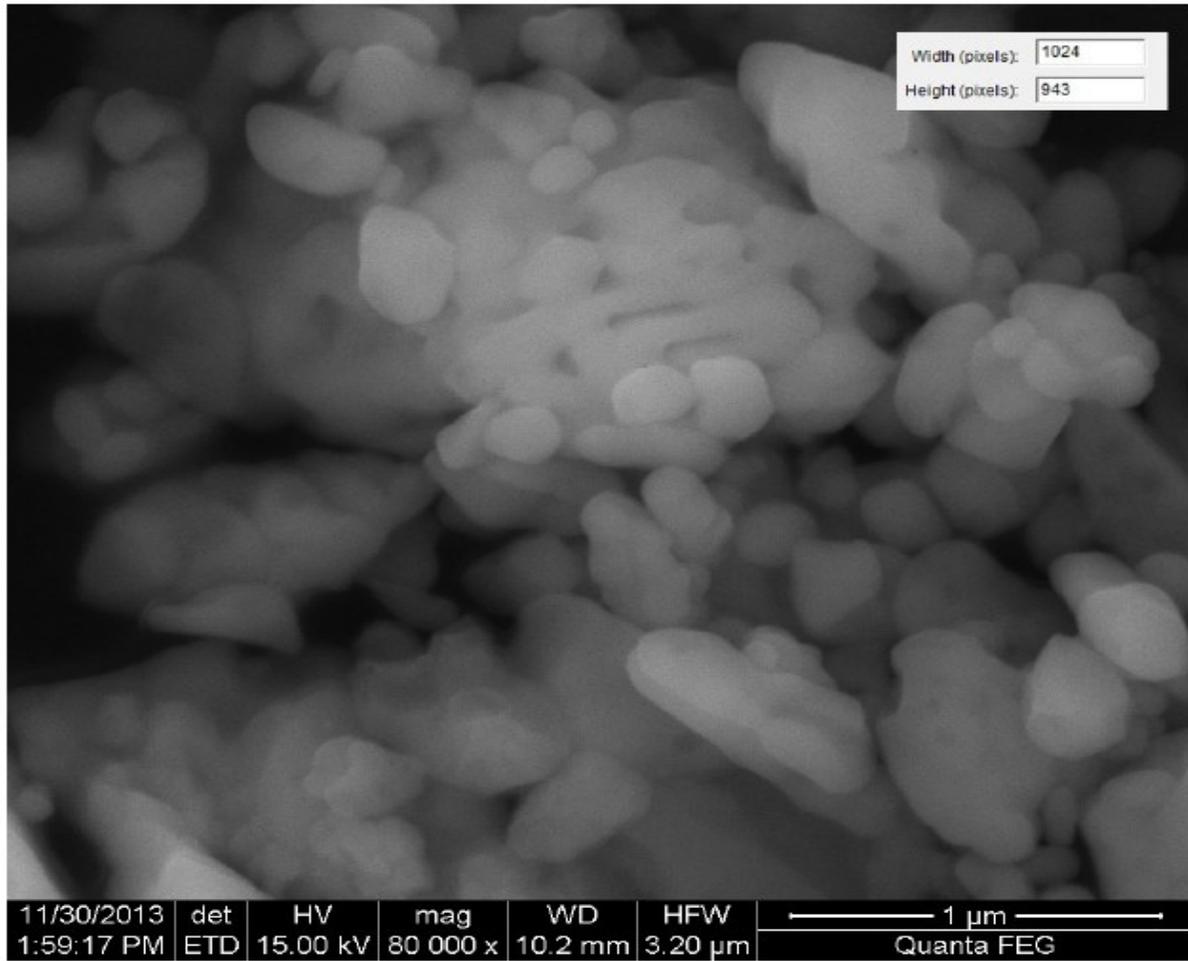


Fig. 33 (a) FESEM image of H_2ZrF_6 powder

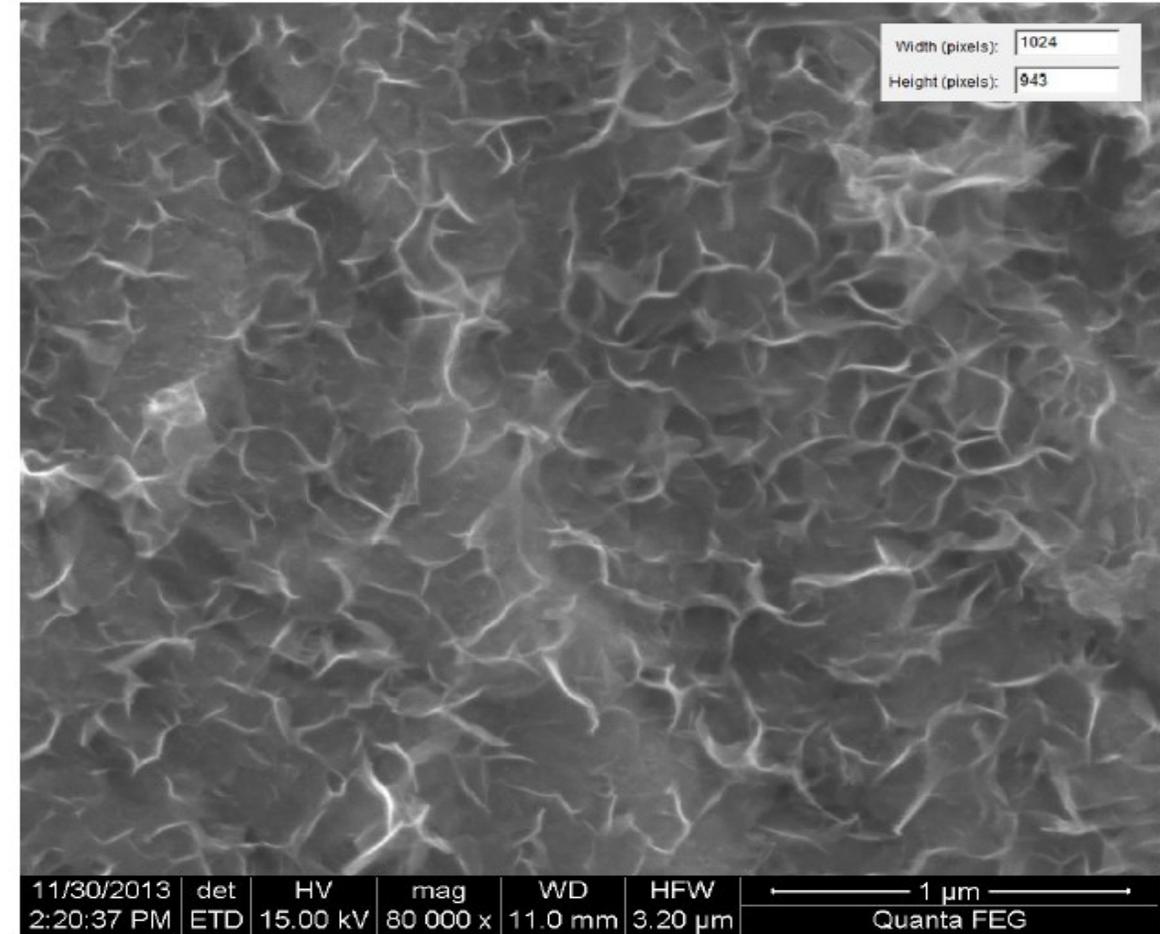
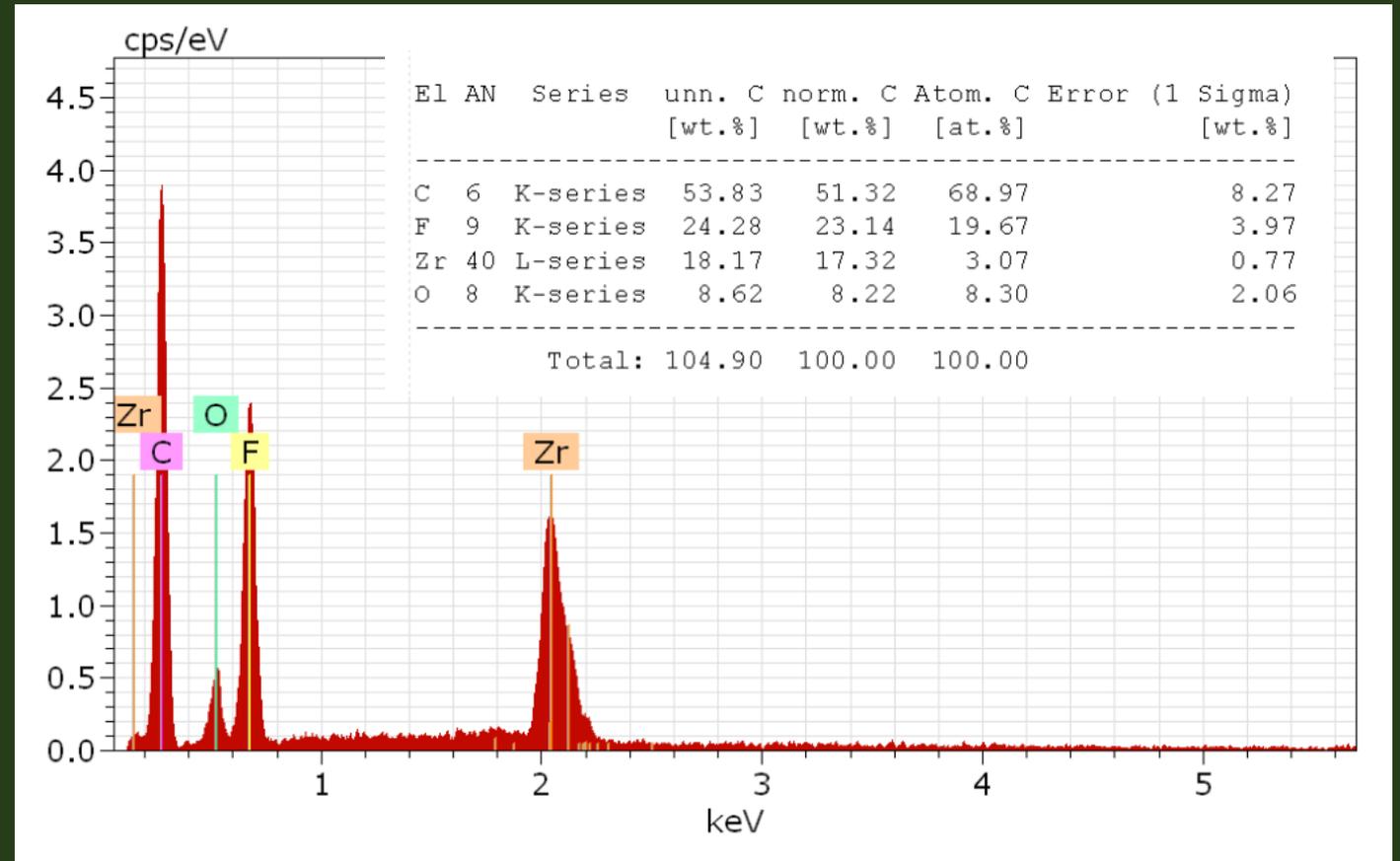


Fig. 33 (b) FESEM image – PNZ treated MS

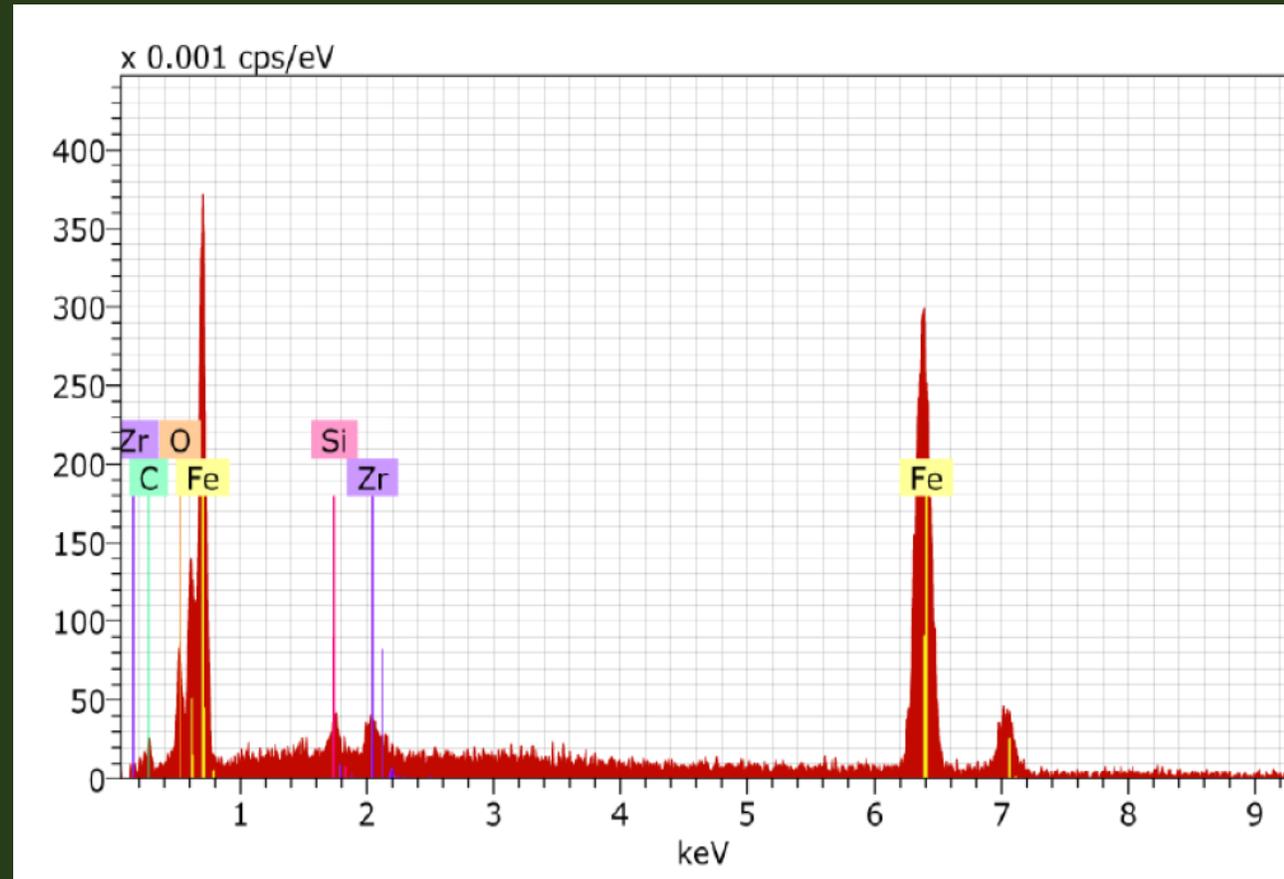
EDAX spectrum of Hexafluorozirconic acid powder

- Size: 20 nm to 50 nm.
- The EDAX spectrum of H_2ZrF_6 powder shows Zr and F peaks at 2.042 keV and 0.676 keV respectively, besides C and O peaks.
- The absence of Si peak indicates the purity of powder form of Hexafluorozirconic acid.



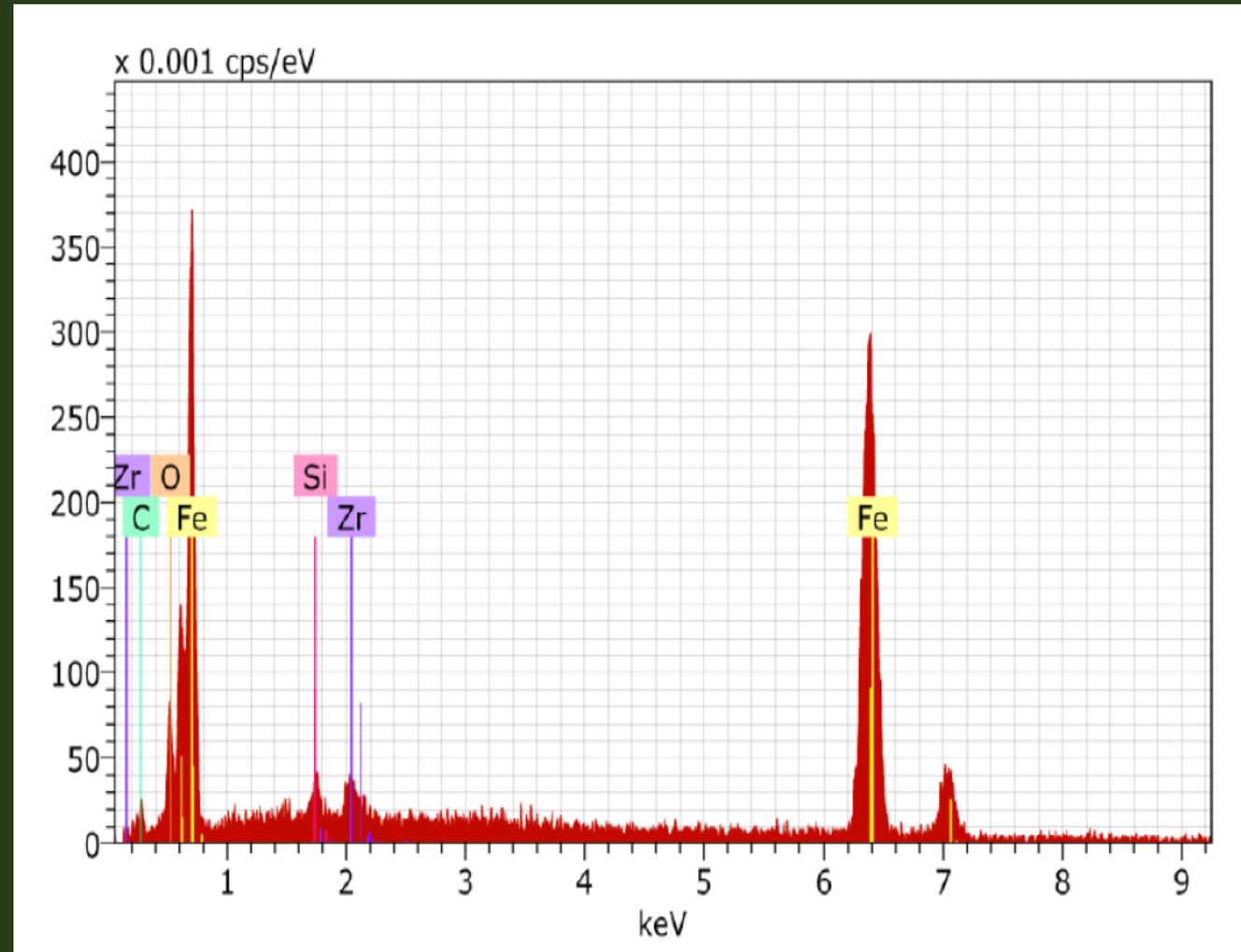
EDAX Spectra of PNZ Coated MS Panel

- A large amount of Fe - due to MS substrate
- Other peaks of O, Zr, Si and a trace of carbon of PNZ coated MS panel (Fig. 33B) may be attributed to the mild steel substrate in PNZ coating with other peaks of O, Zr, Si and a trace of carbon. The EDAX peaks at 0.615 keV, 0.705 keV, 6.404 keV, and 7.057 keV represent Fe(L1), Fe (La1), Fe (Ka1) and Fe (Kb1) respectively.
- Intensities of the peaks at 0.151 keV, 1.792 keV, and 2.042 keV - Zr (Mz), Zr (L1) and Zr (La1)
- Very weak due to very low concentration of Zr.
- The F peak at 0.676 keV also very weak

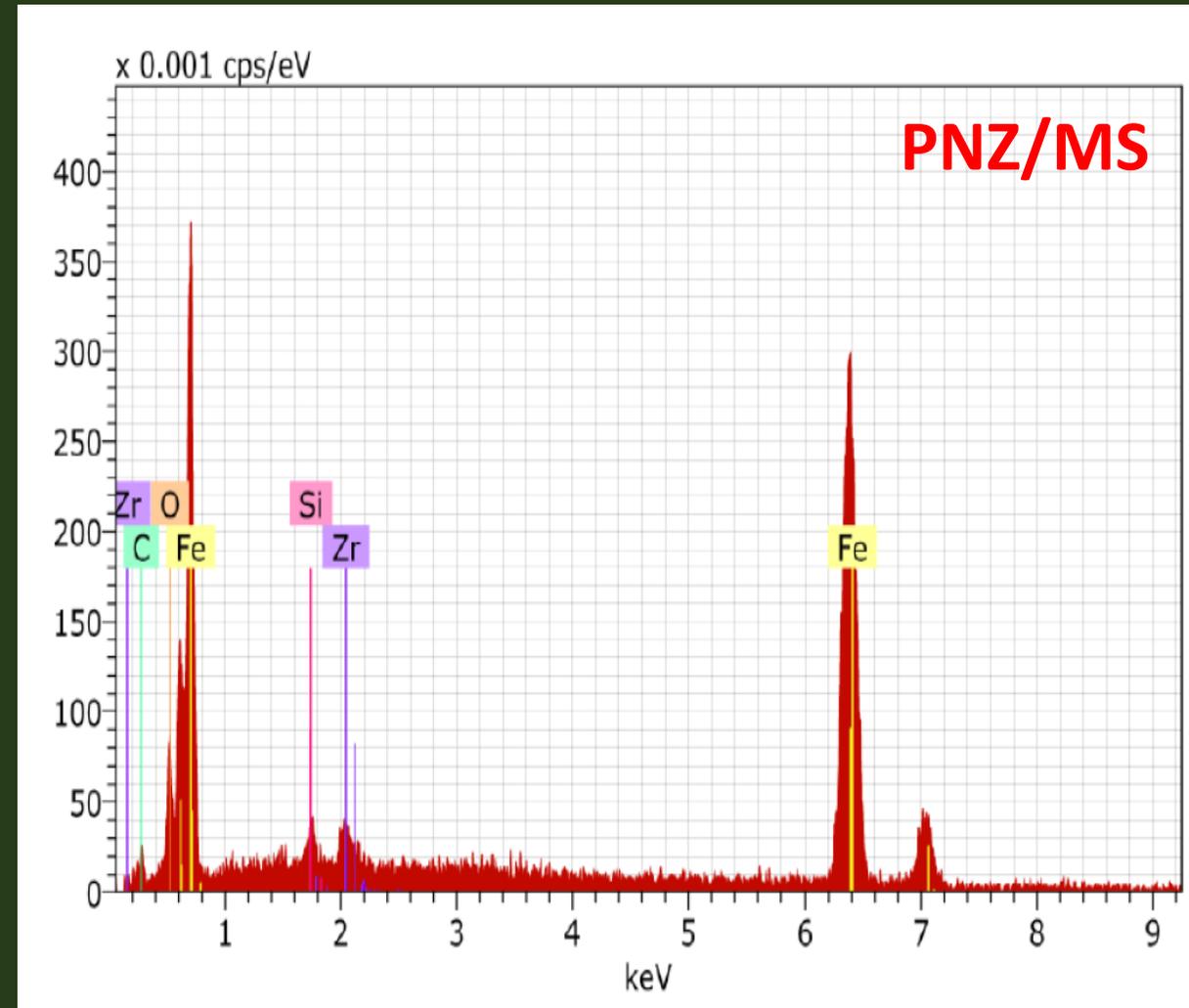
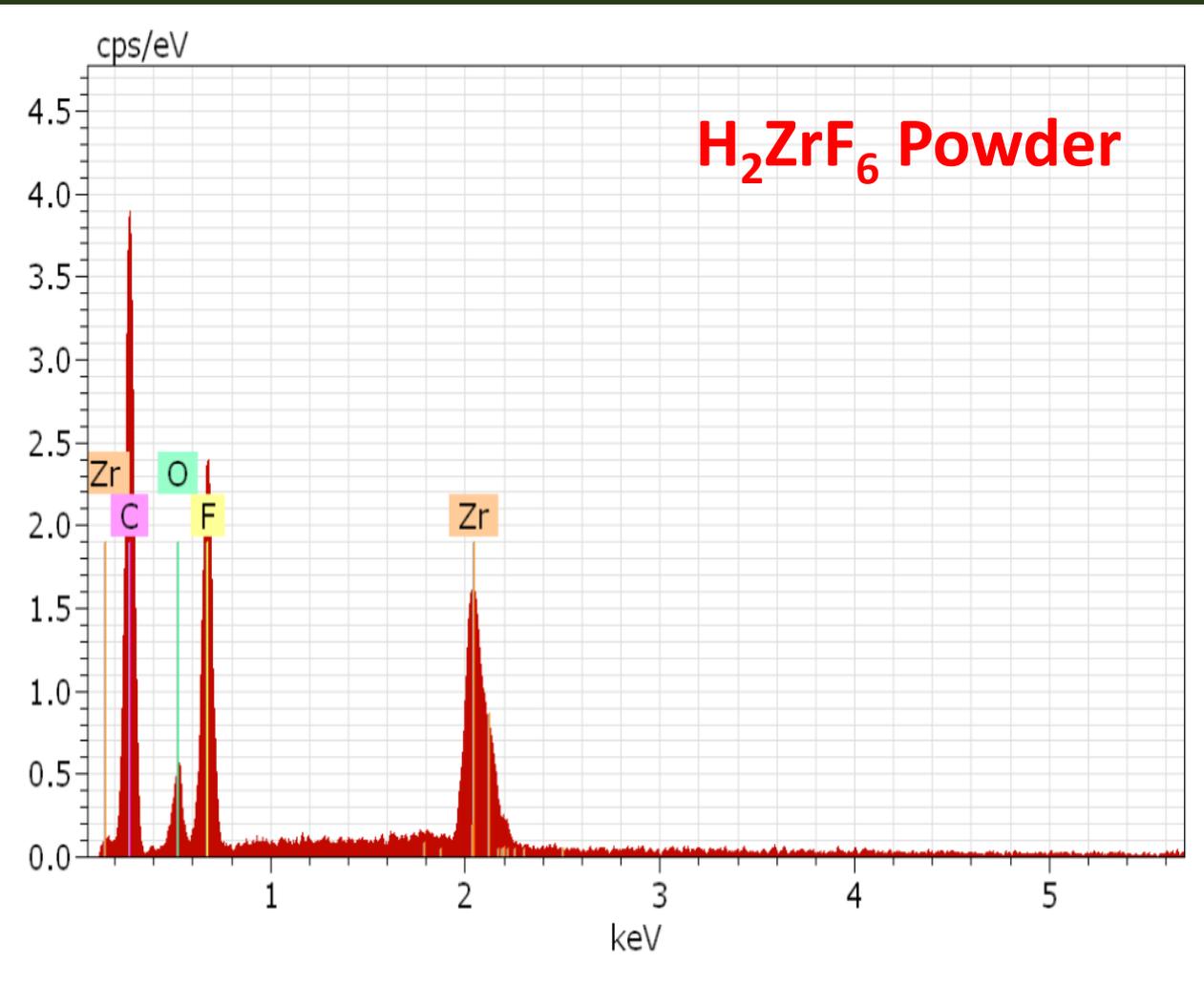


FESEM and EDAX Studies

- Intense peak of F of H_2ZrF_6 powder diminished in the spectrum of PNZ coated MS panel (Fig. 33B) may be attributed to the mild steel substrate in PNZ coating with other peaks of O, Zr, Si and a trace of carbon.
- A trace of F present on the thin film of PNZ on MS.
- An intense peak of O (Ka1) at 0.525 keV due to the oxide film of Zr.
- The Fe and Si peaks absent in the EDAX spectrum of Hexafluorozirconic acid.



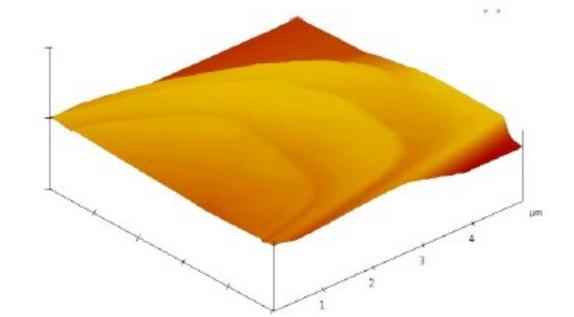
EDAX spectra of H₂ZrF₆ Powder and PNZ coating on MS



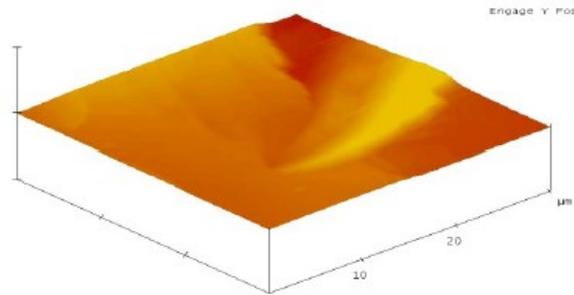
AFM ZnP



Fig.9 Zinc phosphate coating formed on the mild steel



(a) 3D View



(b) Rescanned on the same spot
Fig.10 AFM Images of zinc phosphate treated MS

NZ

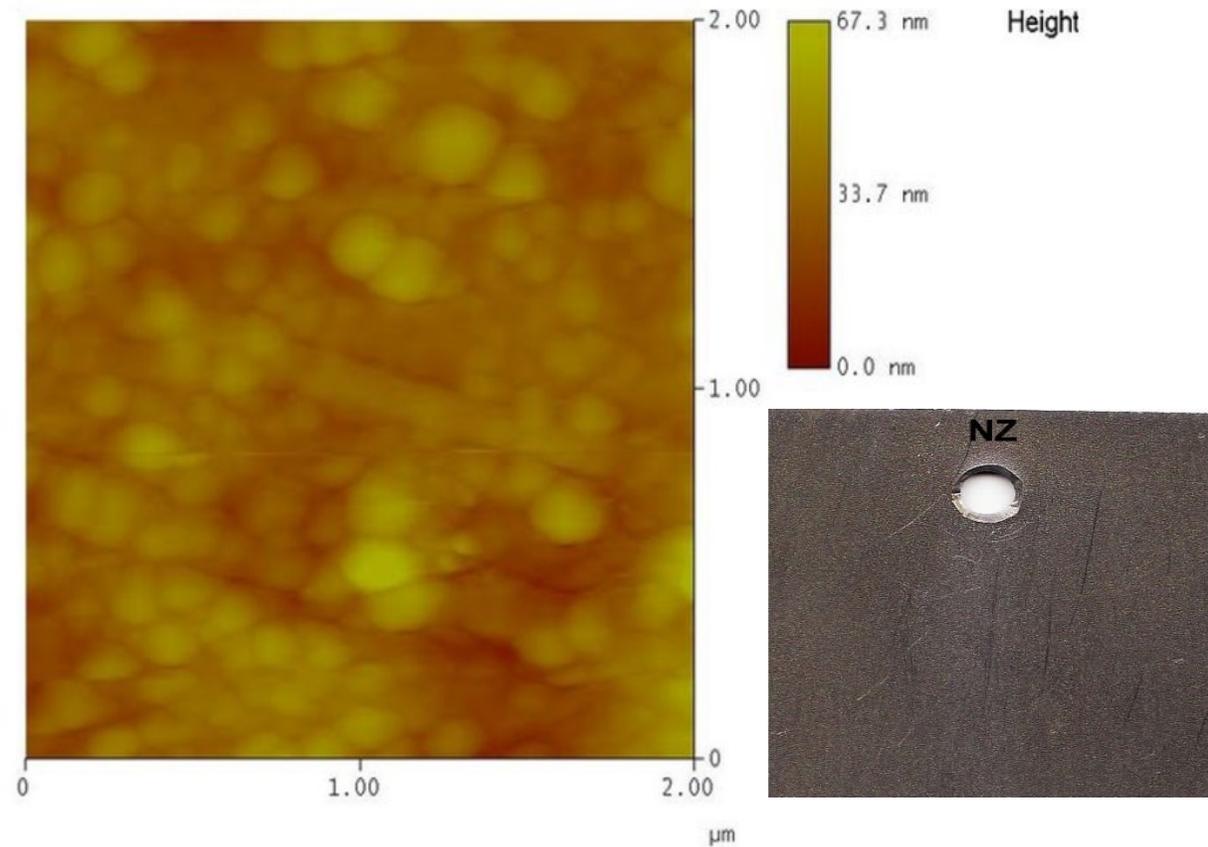


Fig.25 AFM image of NT coating.

AFM

ZnP

NZ

- Uniform striations – petals – Hopeite, Needles - phosphophyllite
- Different patterns on rescanning on the same path
- Very soft - reason for nail marking
- Z (Peak valley height) = 4.309 μm .
- Rq (Root mean square roughness) = 834.47 nm.
- Ra (average grain size) = 675.31 nm.
- Coating thickness = 2.15 μm .
- Ref Van Roy et al reported the phosphate crystallite size in the order of 7-8 nm thickness.
- 0.1 – 0.3 μm in length from AFM measurements [Nanda et al].

- Many clusters of globules - Ostwald's ripening [Bhar et al].
- Z = 67.300 nm
- Rq = 24.445 nm
- Ra = 19.420 nm.

Dry Film Characteristics



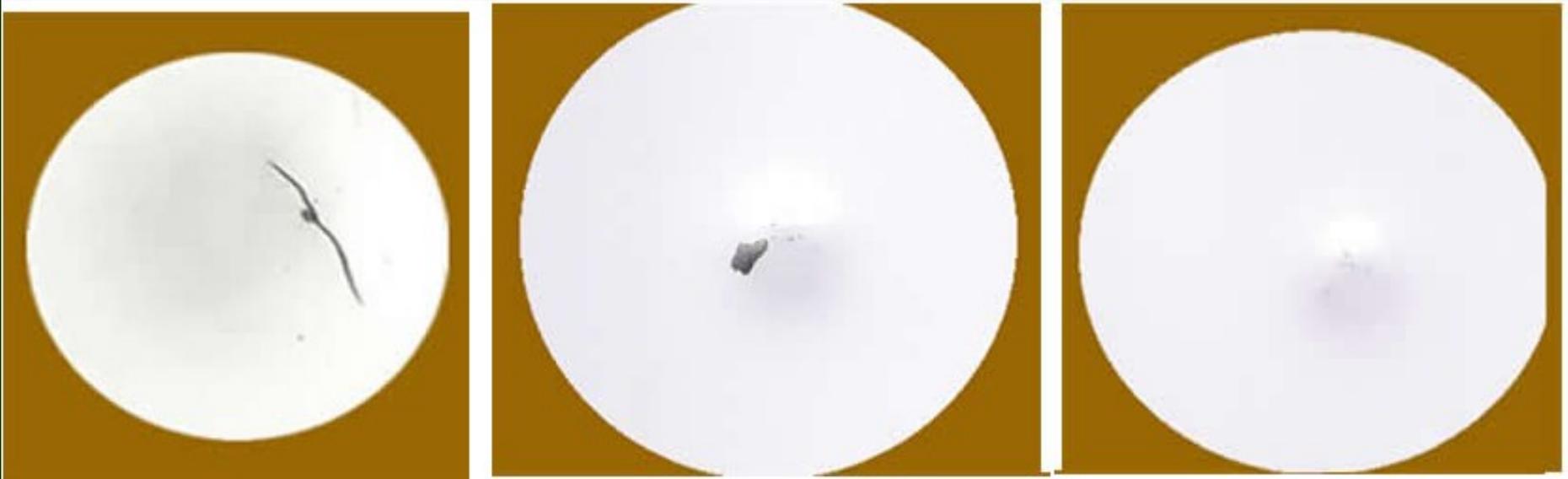
Epoxy Amide Painted Panels
MB – MS Bare Metal
AB – Aluminium Bare Metal
GB – GI Bare Metal
MZ – MS NZ Coated
AZ – Al NZ Coated
GZ – GI NZ Coated

Poly ester epoxy Powder Coat
MZ – MS NZ Coated
AZ – Al NZ Coated
GZ – GI NZ Coated

NOTE:

Powder coat not applied on bare metal panels

Impact Resistance



EPF/UT

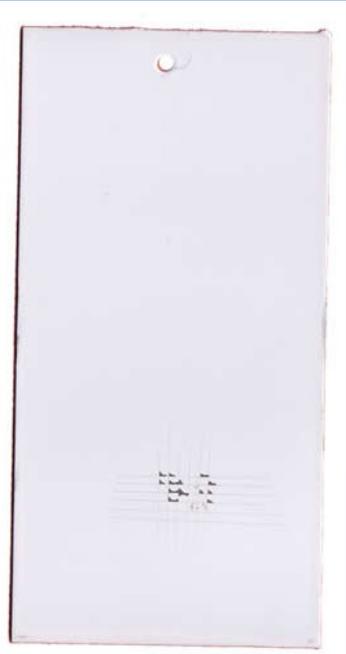
EPF/NZ

PEP/NZ

Cross Hatch Test



EPF/UT

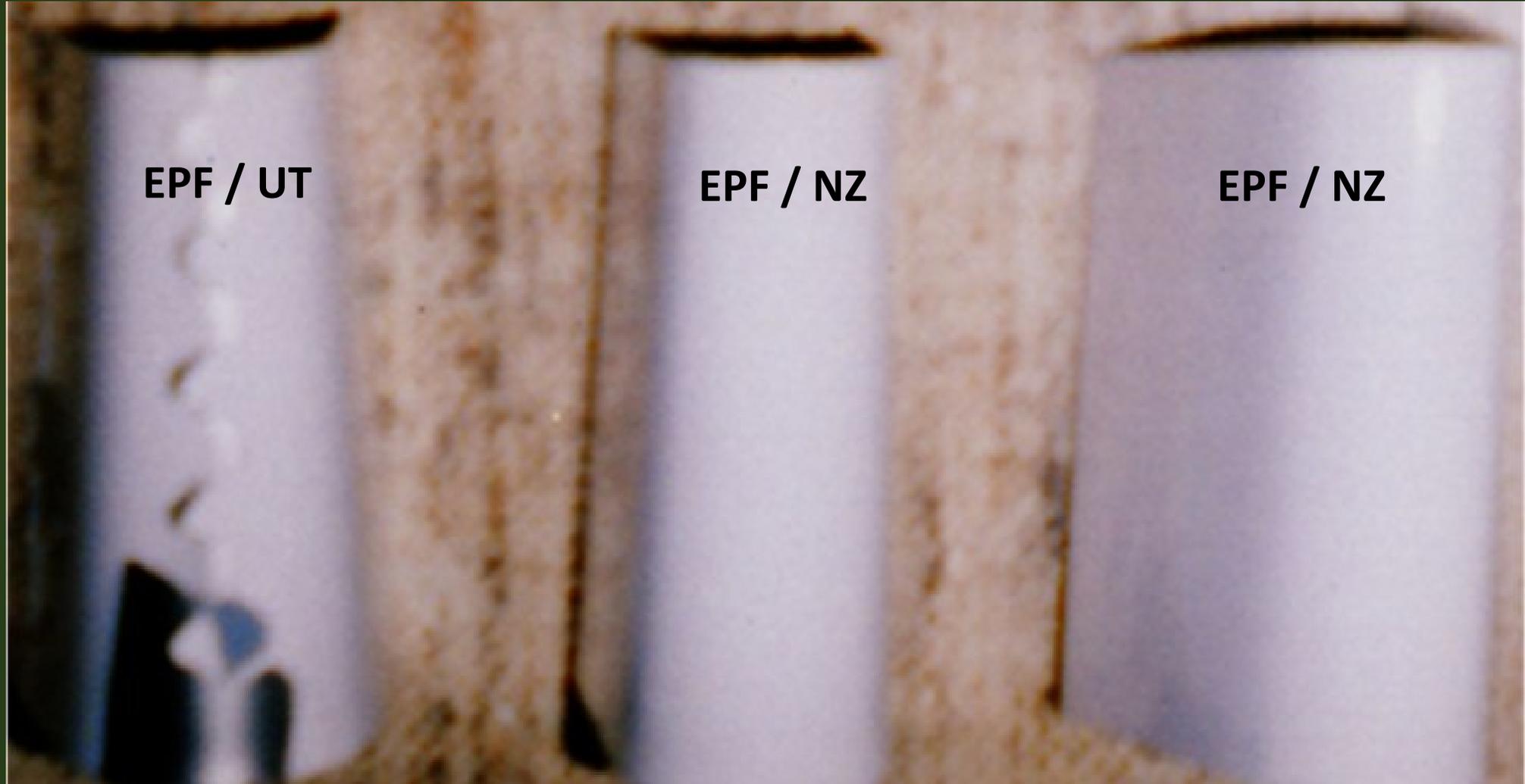


EPF/NZ



PEP/NZ

Bend Test



Salt Spray Resistance – 400 h



Dry Film Characteristics of PEP on NZ Treated Panels

Acid resistance	No blisters
Alkali resistance	No blisters
Water resistance	No blisters
Pencil hardness	3H
Cross hatch test and adhesive tape pull off	Cut portions intact
Bend test	No cracking
Impact resistance	No cracking
Humidity resistance (72 h)	No rust and no blisters
Salt spray resistance (400 h)	No creeping corrosion, no blisters on X-mark

Dry Film Characteristics of PEP on NZ Treated Panels

Acid resistance	No blisters
Alkali resistance	No blisters
Water resistance	No blisters
Pencil hardness	3H
Cross hatch test and adhesive tape pull off	Cut portions intact
Bend test	No cracking
Impact resistance	No cracking
Humidity resistance (72 h)	No rust and no blisters
Salt spray resistance (400 h)	No creeping corrosion, no blisters on X-mark

Dry Film Characteristics

- Nanocoated panels finished with liquid paint gives better performance compared to that of zinc phosphate coated panels and solvent cleaned panels finished with liquid paint in terms of
 - ✓ creeping corrosion resistance
 - ✓ blister resistance
 - ✓ no peeling off of paint film even after 400 hours of salt spray.
- The coating performance is much superior over the **nanocoated panels finished with polyester powder coating** than that of zinc phosphate coated panels finished with polyester powder coating.

Dry Film Characteristics

Table – 29 Dry film characteristics of PUW and PUC on untreated and PNZ treated copper

Tests	PUW		PUC	
	UT	PNZ	UT	PNZ
Acid resistance	Good	Good	Good	Good
Alkali resistance	Good	Good	Good	Good
Water resistance	Micro blisters	Good	Micro blisters	Good
Boling water resistance	Micro blisters	Good	Micro blisters	Good
Diesel resistance	Good	Good	Good	Good
Pencil hardness	H	H	H	H
Cross hatch	Slightly affected	Passed	Slightly affected	Passed

Dry Film Characteristics

Bend test	Failed	Passed	affected Slightly affected	Passed
Impact resistance	Paint film cracked and peeled off	Passed	Paint film cracked	Passed
Humidity resistance (72 h)	Mild rust and blisters	No rust and no blisters	Mild rusts and blisters	No rusts and no blisters
Salt spray resistance (400 hours)	Mild rust; medium size blisters on X-mark	No rust; no blisters on X mark	No rust and no blisters on X-mark	No rust and no blisters on X-mark

PUW: Polyurethane white paint, PUC: Polyurethane clear coat; UT: Untreated copper; PNZ: Nano coated copper

PU Clear Coat on PNZ Treated Kalasams Copper and Brass



Fig. 55 PNZ/PU Clear coated Kalasams ready for delivery

- Temples renovated once in 12 years, renovated along with the temple gopuram (tower) with kalasams.
- kalasams act as lightning conductors for tall temple towers
- Its unique design and copper or copper based alloy.
- 16 Kalasams brought from a temple near Namakkal for renovation after 48 years!!

Contd..



Fig. 48 Condition of the kalasam components before treatment



Fig. 49 Condition of a part of a brass kalasam of Indian Temple Tower before treatment

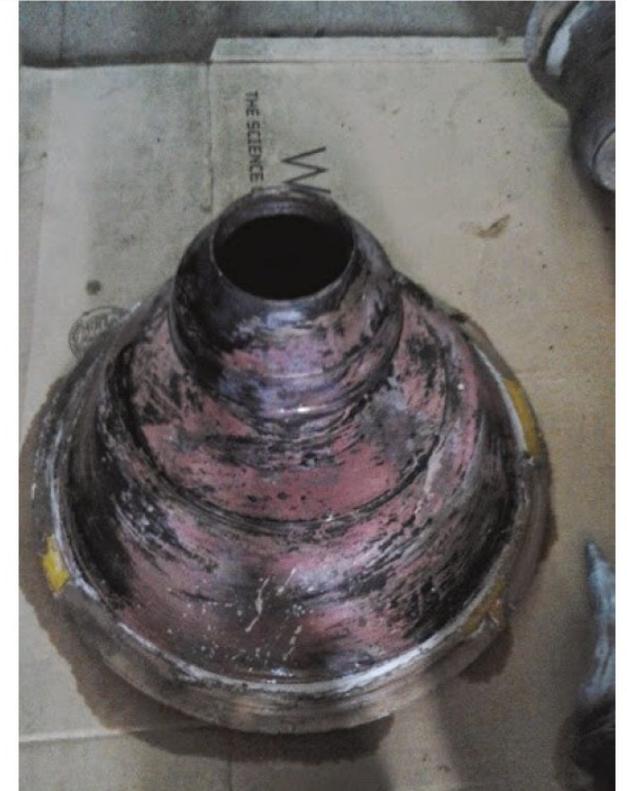


Fig. 50 Copper component of Indian temple tower kalasam before treatment

Contd..



Fig. 51 Polished component of the brass kalasam component



Fig. 52 Polished copper component of Indian temple tower kalasam

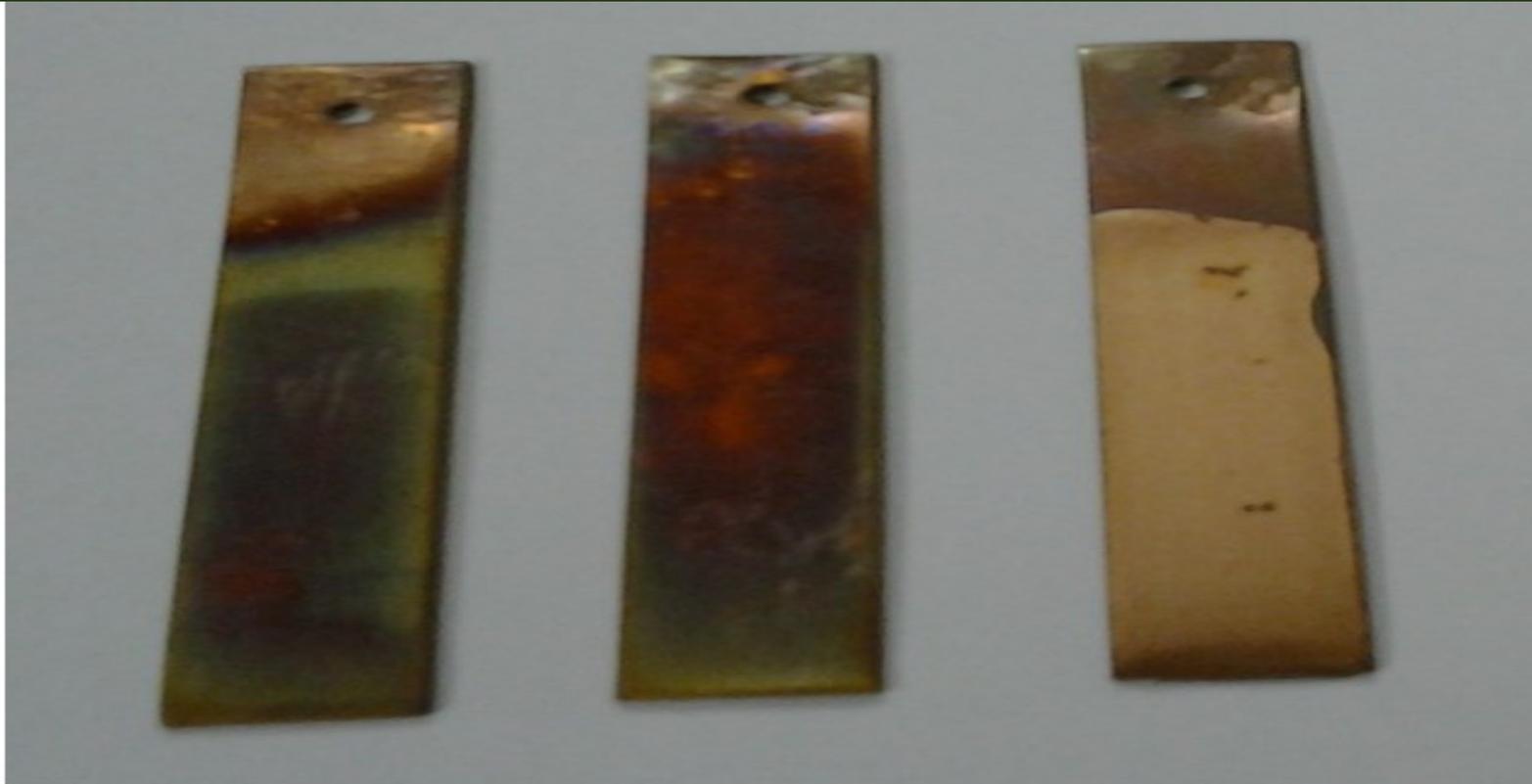
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Fig. 53 PNZ Treatment on Indian temple tower kalasam



PU Clear Coating On PNZ Treated Panels made of Copper and Brass



Left: PUC/ Cu; Middle: Uncoated and untreated Cu; Right: PUC/PNZ/Cu

Fig. 56 PU Clear coat on Cu with and without PNZ treatment after 600 h exposure to neutral salt spray

Antifouling Studies

- Factors involved in algal growth
- Temperature, pH, roughness, medium.
- Zarrouk's medium for the green *Arthrospira* algae
- Bold Basal medium for green *Chlorella* algae
- F/2 medium for marine *Amphora* algae .
- The roughness of a surface allows the algal growth freely.
- The MS panels have no remarkable difference between the nano treated and untreated surface
- Due to overall surface smoothness of metal.

NCu

Bare



Fig. 59 MS Panels kept in (A) *Arthrospira platensis*; (B) *Chlorococcum humicola*; (C) *Amphora coffeaeformis*. L: Nano-treated panels, R: Control panels

Algal Growth on Wooden Panels

NCu Bare



Fig. 61 Wooden Panels kept in (A) *Arthrospira platensis*; (B) *Chlorococcum humicola*; (C) *Amphora coffeaeformis*. L: Nano-treated panels, R: Control panels

- Considerable growth of algae on the untreated wooden panels.
- Algal growth measured via chlorophyll-a concentration and cell counts monitored

Algal Growth – Different stages

- Considerable growth of algae on the untreated cement panels.
- Four stages of algae growth:
 - lag phase – initial phase
 - log phase – high cell multiplication
 - stationary phase – growth maintained
 - death phase – due to lack of nutrients.

Cell counts of nano coated and uncoated panels

- Arthrospira – [Wood (~95%) > Mild steel (~93%) > Cement slab (~90%)]
- Amphora – [Wood (~90%) > Mild steel (~88%) > Cement slab (~85%)]
- Chlorella – [Wood (~85%) > Mild steel (~83%) > Cement slab (~80%)].

NCu

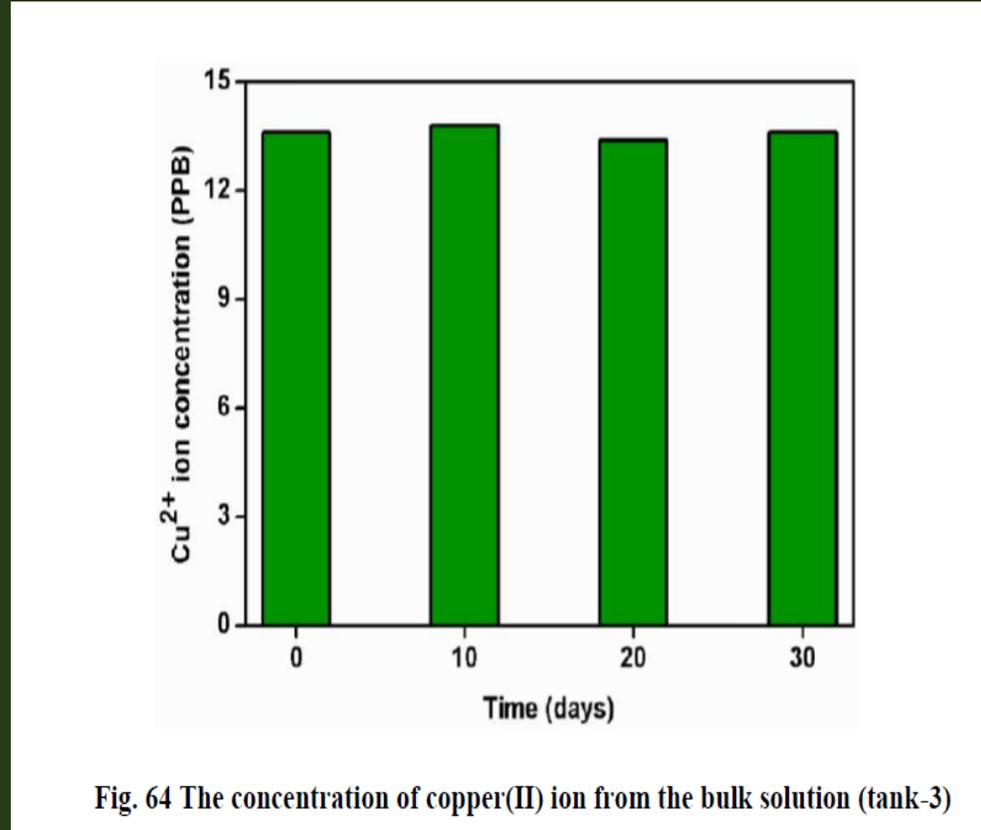
Bare



Fig. 60 Cement Panels kept in (A) *Arthrospira platensis*; (B) *Chlorococcum humicola*; (C) *Amphora coffeaeformis*. L: Nano-treated panels, R: Control panels

Measurement of the Concentration of Copper

- Measured by ICP spectrometry at different time intervals.
- The concentration of Cu^{2+} ion in the bulk solution
- No difference in Cu^{2+} ion concentration from zero to thirty days in the bulk solution.
- The ICP values confirm the absence of additional Cu^{+2} which indicate that the originally added nutrient of copper(II) salts for the algal growth was only present in the tank
- The copper NPs not leached out from the coated panels
- The CDC NPs adhere strongly on to the surface of the panels.



Proposed Mechanism for Antifouling Behaviour

1. Accumulation and dissolution of NPs in the bacterial membrane
 - a) changing its permeability
 - b) subsequent release of lipopolysaccharides, membrane proteins and intracellular biomolecules
 - c) dissipation of the proton across the plasma membrane
2. Generation of reactive oxygen species (ROS) or/and their corresponding ions from NPs
 - a) subsequent oxidative damage to cellular structures
3. Uptake of metallic ions derived from NPs or of NPs as whole into cells
 - a) Depletion of intracellular ATP production
 - b) Disruption of DNA replication

4. Summary & Conclusion

- Anticorrosion Studies
- Antifouling Studies
- Two types of metal pretreatment
 - Conventional zinc phosphate coating on MS
 - Nano-zirconia coating on MS, GI, Cu, Glass, Wood, Slate Stone, Cement Panels
- Nano zirconia coating a better candidate than zinc phosphate coating
 - Less sludge formation in the bath
 - Room temperature
 - Quick processing time
 - Less consumption of energy
 - Cost reduction of sludge disposal
 - Less environmental pollution.

4. Summary & Conclusion

Summary & Conclusion

- Powder based Nanozirconia coating (PNZ) was developed using Hexafluorozirconic acid powder as an equivalent product to the commercial Bonderite NT-1.
- **Project Launched in 2015 at Vitraquim in Mexico using PNZ**
- The PNZ coating studied on copper and found to improve the adhesion of polyurethane clear coat to protect the natural color and luster of copper.
- The role of copper nanoparticles in the top coat was studied in antifouling application on various substrates such as MS, GI, wood, and cement panels.

Summary & Conclusion

- Zirconia coating for base coat enhances anticorrosion, humidity resistance, hardness, flexibility and adhesion of top coat.
- Polyester epoxy powder coat gives the best result with Nanozirconia coating.
- Being a transparent adhesion promoting coating NZ is ideal for clear coats on aluminium, copper, silver and brass.

Summary & Conclusion

- ❑ Nanozirconia / epoxy amide liquid paint – better performance
 - creeping corrosion resistance
 - blister resistance
 - no peeling off of paint film even after 400 h SSR
- ❑ Nanozirconia / polyester powder coating
 - Overall performance
 - A successful combination in the Turnkey Projects
- ❑ PNZ – a better candidate than NZ
 - Transportation Powder form of NZ
 - Handling
 - On-site Bath make up



भारत सरकार
GOVERNMENT OF INDIA
पेटेंट कार्यालय
THE PATENT OFFICE
पेटेंट प्रमाणपत्र
PATENT CERTIFICATE
(Rule 74 Of The Patents Rules)

पेटेंट सं. / Patent No. : 346961
आवेदन सं. / Application No. : 5944/CHE/2013
फाइल करने की तारीख / Date of Filing : 19/12/2013
पेटेंटी / Patentee : THE REGISTRAR

प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित NANOTRICATION TRANSPARENT CONVERSION COATING FOR COPPER नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 19th day of December 2013 से बीस वर्ष की अवधि के लिए पेटेंट अनुदत्त किया गया है।

It is hereby certified that a patent has been granted to the patentee for an invention entitled NANOTRICATION TRANSPARENT CONVERSION COATING FOR COPPER as disclosed in the above mentioned application for the term of 20 years from the 19th day of December 2013 in accordance with the provisions of the Patents Act, 1970.

INTELLECTUAL
PROPERTY INDIA
PATENTS | DESIGNS | TRADE MARKS
GEOGRAPHICAL INDICATIONS



अनुदान की तारीख : 17/09/2020
Date of Grant :

पेटेंट नियंत्रक
Controller of Patent

OKrupla

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, 19th day of December 2015 को और उसके पश्चात प्रत्येक वर्ष में उसी दिन देय होगी।
Note. - The fees for renewal of this patent, if it is to be maintained will fall / has fallen due on 19th day of December 2015 and on the same day in every year thereafter.

Nanotrication Transparent Conversion Coating for Copper Granted Patent

Thanks to
Registrar,
Dr. Balasubramanian
UOM

Nanoceramic Coating Project Launched in 2015 at Vitraquim in Mexico



**Thanks to
Mr. Carlos Sacal
Director
Vitraquim**

Nanozirconia Pretreatment and Powder Coat Plant Turnkey Project Launched in 2018 at Wittur Elevators, Sriperumbudur, Tamilnadu



Thanks to
Mr. Suraj
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Wittur
Elevators

List of Publications

- Nano-Zirconia Coating on Mild Steel with the Top Coats of Polyester Epoxy Powder and Amide Cured Epoxy Liquid Paints, E. Ramanathan, S. Balasubramanian, [Prog. Org. Coat.](#) 2016, 93, 68-76.
<http://dx.doi.org/10.1016/j.porgcoat.2016.01.007>
- Synthesis and characterization of hexafluorozirconic acid and its coating application on mild steel, E. Ramanathan, S. Balasubramanian, [Surf. Coat. Technol.](#), 2016, 304, 228-236
- Synthesis of chitosan capped copper oxide nanoleaves using high intensity (30KHz) ultrasound Sonication and their application in antifouling coatings , T. Abiraman, G. Kavitha, E.Ramanatahn, R. Rengasamy and S. Balasubramanian, [Ultrason. Sonochem.](#)2017, 34,781-791

List of Publications

- **Nanotrication transparent conversion coating for copper**, S. Balasubramanian, E. Ramanathan, Indian patent, Journal Publication No. 02 /2014, 5944/CHE/2014, dt.19/12/2013.
- **A process for making nano- zirconia coated mild steel for industrial applications**, S. Balasubramanian, E. Ramanathan, Indian patent, Journal Publication No. 24/2013, 1058/CHE/2013, dt. 14/06/2013.2
- **Synthesis of Hexafluorozirconic acid powder and its Nano conversion coating for ferrous and non-ferrous metal components**, S. Balasubramanian, E. Ramanathan, Indian patent, Journal Publication No. 4607/CHE/20141

Conferences

- Determination of coating thickness of zinc phosphate coating by electrochemical impedance spectroscopy, E. Ramanathan, I.M. Bilal, S. Balasubramanian, Seventeenth National Convention of Electrochemists (NCE-17), Chennai 14-15, Sep-2012.
- Nanoceramic coatings for industrial applications, S. Balasubramanian and E. Ramanathan, Villa conference on Interaction among Nanostructures(VC-IAN), Orlando, Florida, USA, Feb 3-7, 2008.
- Comparative study of electroless nanoceramic coating and zinc phosphate coating in metal pretreatment, E. Ramanathan, K. Rajasekaran, S. Balasubramanian, ASPUM, International Symposium on Science in New Millennium, University of Madras, 12-13th, June 2006.

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