

Effect of hydrodynamics on copper-nickel alloy rotating disc electrode in marine environment

K. Chaitanya Kumar^{a*}, B. V. Appa Rao^b, S. Srinivasa Rao^c, K. Vimal Kumar^b

^aCorrosion & Fouling Division, Corporate R&D Centre, Bharat Petroleum Corporation Ltd.,
Greater Noida – 201 306, Uttar Pradesh, India.

^bDepartment of Chemistry, National Institute of Technology Warangal – 506 004, Telangana,
India.

^cDepartment of Chemistry, V. R. Siddhartha Engineering College (Autonomous),
Vijayawada –520 007, Andhra Pradesh, India.

*Corresponding author Email: *chaitanyakanukula@gmail.com*

S.1. Surface analysis by X-ray photoelectron spectroscopy

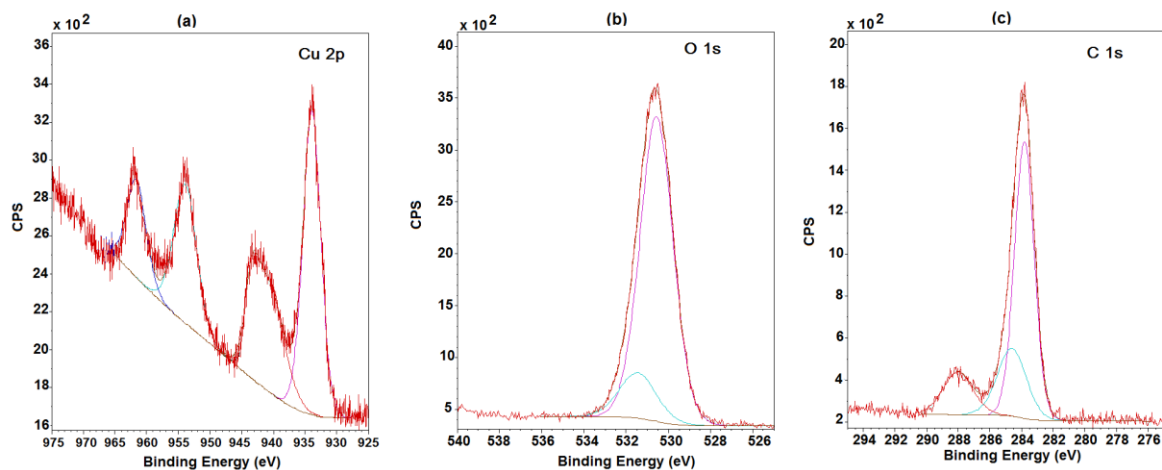


Fig. S1. XPS deconvolution spectra of (a) Cu 2p, (b) O 1s and (c) C 1s of Cu90–Ni10 alloy in synthetic seawater at 2200 rpm after 48 h immersion period.

The XPS deconvolution spectra of Cu 2p, O1s and C1s of Cu90–Ni10 alloy in seawater at 2200 rpm after 48 h immersion period is shown in Fig. S1. Cu 2p, shown in Fig.S1a, exhibits the Cu 2p_{3/2} peak at 933.9 eV along with a shake–up satellite at 943.3 eV. These peaks are

normally assigned to the presence of Cu(II) species ^{1,2}. However, in the present case, there must be some amount of Cu(I) also as the oxidation of Cu(0) to Cu(I) occurs first followed by oxidation of Cu(I) to Cu(II). The O 1s deconvolution spectrum (Fig.S1b) exhibits a high intensity peak at 530.6 eV and a low intensity one at 531.5 eV. The former peak is assigned to mainly CuO and small amount of Cu₂O while the later one is assigned to Cu(OH)₂ ³. From these results it can be inferred that the surface film after corrosion of the alloy in synthetic seawater is composed of CuO, Cu(OH)₂ and Cu₂O. The C 1s peaks (Fig. S1c) at 283.9 eV, 284.6 eV and 288.0 eV are due to contaminant carbon, which is likely due to cracking of vacuum oil used during the operation of XPS instrument ⁴. Similar type of results are also observed in Cu90–Ni10 alloy in seawater polluted with 10 ppm sulphide, which are depicted in Fig. S2. In addition to above peaks, S 2p (Fig. S2a) exhibit two different peaks corresponding to sulphide in two different environments. The high intense S 2p_{3/2} peak at 161.5 eV corresponds to Cu₂S^[42] and the other one with less intensity at 162.7 eV represents CuS ^{5,6}. Hence, it is inferred that the surface film after corrosion of the alloy in synthetic seawater is composed of CuO, Cu₂O, Cu₂S and CuS.

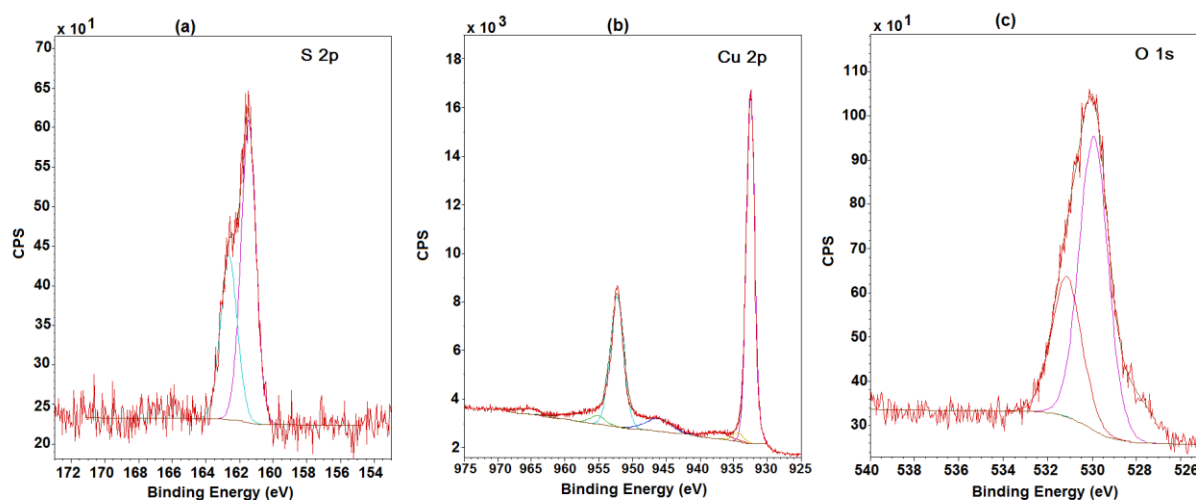


Fig. S2. XPS deconvolution spectra of (a) S 2p, (b) Cu 2p and (c) O 1s of Cu90–Ni10 alloy in synthetic seawater containing 10 ppm sulphide at 2200 rpm after 48 h immersion period.

In the XPS survey spectrum of the film formed on Cu–Ni (90/10) alloy in synthetic seawater containing 6.5 mM APT at 2200 rpm after 48 h immersion period, the peaks due to copper, carbon, nitrogen and oxygen are detected. The corresponding computer deconvolution spectra are shown in Figs.23a–d respectively. The XPS exhibited peaks due to N 1s and C 1s, which infer the presence of APT in the surface film. The C 1s spectrum shows three peaks, one at 284.9 eV with high intensity and the other two at 284.1 eV and 286.2 eV with less intensity. The high intense C 1s peak at 284.9 eV is characteristic of carbon present in the aromatic ring of APT ⁷. The less intense C 1s peaks at 284.1 eV and 286.2 eV are due to contaminant carbon ⁸. The N 1s spectrum shows three peaks, one at 399.2 eV and the other two at 398.3 and 400.5 eV. The N 1s peak at 399.2 eV is assigned to ‘C–NH₂’ group ⁹. Another peak at 398.3 eV is due to the presence of ‘–N=C’ in the tetrazole ring ¹⁰. The peak at 400.5 eV is due to the presence of ‘–N–H’ group ¹¹. The Cu 2p_{3/2} peak at 933.5 eV infers the presence of Cu(I) species ¹². Another Cu 2p_{3/2} peak at 934.8 eV along with a shake–up satellite at 943.6 eV infers the presence of Cu(II) species also on the alloy surface. The presence of O 1s peak at 531.8 eV is assigned to CuO or Cu(OH)₂ and Cu₂O, which are formed in small quantities before the formation of the protective film ^{13,14}. These results infer the formation of polymeric complex namely [Cu(I)APT]_n by electrostatic interactions, which is highly protective.

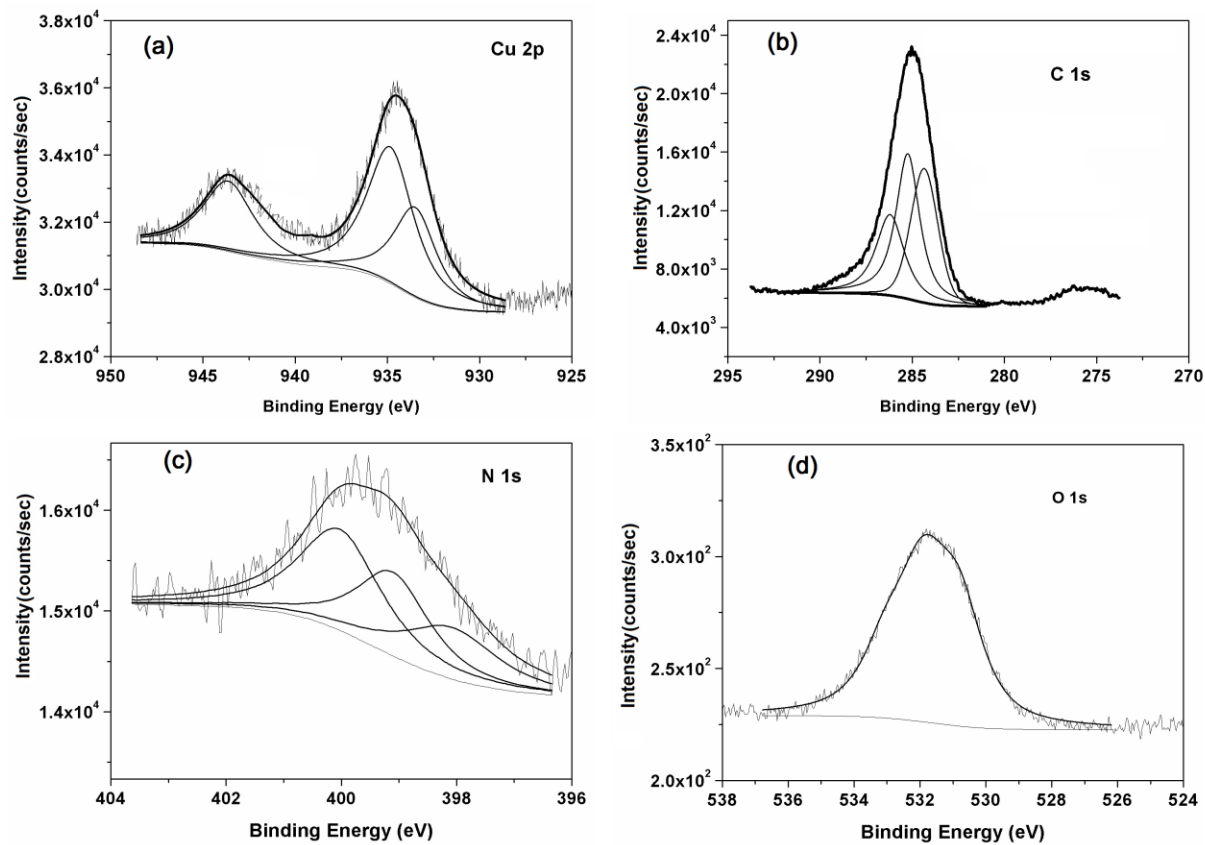


Fig. S3. XPS deconvolution spectra of (a) Cu 2p, (b) C 1s, (c) N 1s and (d) O 1s of Cu₉₀-Ni₁₀ alloy in synthetic seawater in the presence of APT film at 2200 rpm after 48 h immersion period.

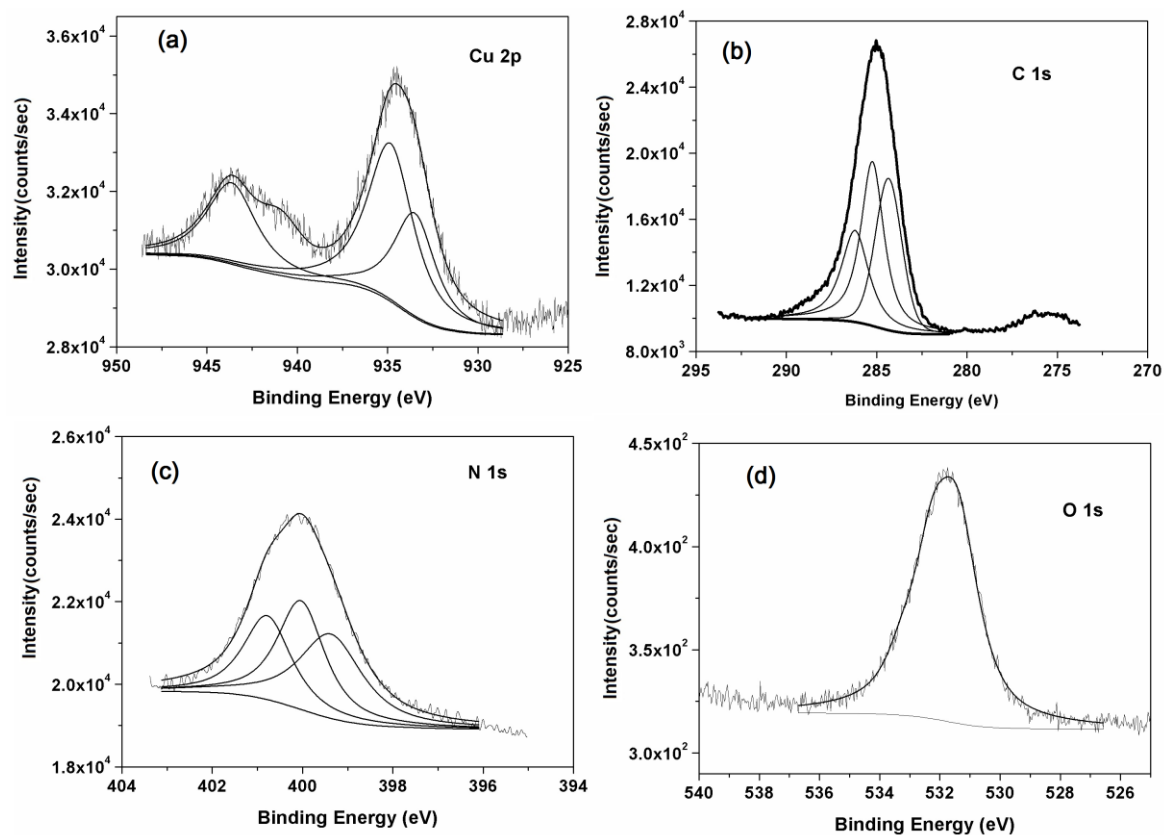


Fig. S4. XPS deconvolution spectra of (a) Cu 2p, (b) C 1s, (c) N 1s and (d) O 1s of Cu90–Ni10 alloy in synthetic seawater containing 10 ppm sulphide in the presence of APT film at 2200 rpm after 48 h immersion period.

Similar peaks are also observed in the case of the film formed on Cu–Ni (90/10) alloy in synthetic seawater polluted with sulphide in the presence of 6.5 mM APT at 2200 rpm after 48 h immersion period and exhibited peaks due to copper, carbon, nitrogen and oxygen. The corresponding computer deconvolution spectra are shown in Figs. 24a–d respectively.. All these results infer that the $[\text{Cu(I)APT}]_n$ polymeric complex protects the alloy from corrosion even at 2200 rpm in seawater and seawater containing sulphide ions.

References

- 1 P. E. Larson, *J. Electron Spectros. Relat. Phenomena*, 1974, **4**, 213–218.
- 2 D. C. Frost, A. Ishitani and C. a. McDowell, *Mol. Phys.*, 1972, **24**, 861–877.
- 3 H. ???H Strehblow and H. ???D Speckmann, *Mater. Corros.*, 1984, **35**, 512–519.
- 4 G. P. Cicileo, B. M. Rosales, F. E. Varela and J. R. Vilche, *Corros. Sci.*, 1999, **41**, 1359–1375.
- 5 G. Kear, B. D. Barker, K. R. Stokes and F. C. Walsh, *Corrosion*, 2009, **65**, 24–36.
- 6 G. W. Poling, *Corros. Sci.*, 1970, **10**, 359–370.
- 7 B. C. Syrett, *Corros. Sci.*, 1981, **21**, 187–209.
- 8 L. E. Eiselstein, B. C. Syrett, S. S. Wing and R. D. Caligiuri, *Corros. Sci.*, 1983, **23**, 223–239.
- 9 W. a. Badawy, K. M. Ismail and A. M. Fathi, *J. Appl. Electrochem.*, 2005, **35**, 879–888.
- 10 W. a. Badawy, K. M. Ismail and A. M. Fathi, *Electrochim. Acta*, 2006, **51**, 4182–4189.
- 11 Y. Z. Wang, A. M. Beccaria and G. Poggi, *Corros. Sci.*, 1994, **36**, 1277–1288.
- 12 P. Druska and H. H. Strehblow, *Corros. Sci.*, 1996, **38**, 1369–1383.
- 13 C. Kato, J. E. Castle, B. G. Ateya and H. W. Pickering, *J. Electrochem. Soc.*, 1980, **127**, 1897–1903.
- 14 J. M. Popplewell, R. J. Hart and J. a. Ford, *Corros. Sci.*, 1973, **13**, 295–309.