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REVIEW ARTICLE

A review of the effects of benzotriazole on the corrosion of copper and copper alloys in clean and polluted environments

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Abstract A continuing challenge in materials design is the achievement of high operational efficiency through improvements in performance criterion, particularly its service life-time characteristics. Benzotriazole (BTAH) has now been in use for many years for the protection of copper and copper alloys against various forms of corrosion. In this review, the chemistry of BTAH and theories regarding its mode of action are summarized. Also, a survey of the reported work in both clean and polluted environments is documented. More interestingly, the adverse effect of BTAH on the corrosion of Cu and Cu alloys in sulfide polluted environments is introduced.

Keywords Copper · Copper alloys · Corrosion · Inhibition · Benzotriazole · Pollution

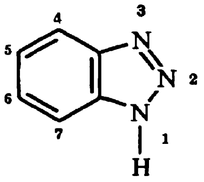
1 Introduction

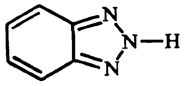
Copper is a metal that has a wide range of applications due to its outstanding properties. This metal can be easily alloyed with other elements to form a great class of materials known as copper base alloys. These alloys have a long history of service in marine environments and saline water systems, e.g., heat exchangers, water distribution systems, water treatment units, and multi-stage flash (MSF) in the desalination plants. These applications can be ascribed to the attractive combination of properties these alloys posses, e.g., good machinability, high thermal and electrical conductivity, and resistance to corrosion and biofouling [1, 2]. The most prominent among copper base alloys have traditionally been brasses (Cu–Zn) and cupronickels (Cu–Ni). Aluminium bronzes (Cu–Al) constitute another important class of copper base alloys, which have better strength and corrosion resistance [3, 4].

Copper and its alloys are resistant toward the influence of atmosphere and many chemicals, however, it is known that these materials are susceptible to corrosion in aggressive media. The use of corrosion inhibitors remains one of the necessary procedures used to protect metals and alloys against attack in many industrial environments [5]. Benzotriazole (BTAH) was shown to be the most effective inhibitor for copper and its alloys in various aggressive environments. Ever since the early works of Cotton and co-workers [6, 7] there has been a continuing interest in the mechanism of inhibition and in various aspects of the interaction of BTAH with the oxide-free and oxide-covered copper surfaces [4, 8–11]. The aim of the present review is to briefly summarize and document the reported literature dealing with the use of benzotriazole to inhibit the corrosion of copper and its alloys in different environments.

2 Benzotriazole: its chemistry and mode of action

Benzotriazole (BTAH) is an organic compound consisting of benzene and triazole rings with a formula of $C_6H_5N_3$ which can exist in the following tautomeric forms [12]:





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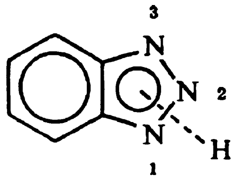
More accurately, BTAH can be represented using the resonating form:



This last structure shows that BTAH can act as a weak acid by releasing a proton or a base by accepting a proton to one of the nitrogen lone pairs of electrons. On the other hand, BTAH can utilize the lone pairs of electrons existing on nitrogen atoms to bond itself to copper surface. In this way, a coordination compound can be formed on the copper surface which can act as an inhibitor against corrosion. This makes benzotriazole one of the most efficient inhibitors for the corrosion of copper and its alloys in aqueous media [13–20]. Generally, BTAH acts as an anodic corrosion inhibitor [21–27] via its physisorption [22, 23] on the copper surface that follows, in most cases, Langmuir isotherm [21, 22, 25, 28–30]. However, it was shown in some other cases that BTAH can act as a mixed (i.e., anodic and cathodic) type inhibitor [23].

Two mechanisms have been proposed to account for the high inhibiting efficiency of BTAH in aqueous electrolytes. The first attributes it to adsorption of BTAH on the (single- as well as poly-crystalline) copper surface, i.e.,

$$[\mathrm{BTAH}]_{\mathrm{aq}} + \mathrm{Cu}_{(\mathrm{s})} = [\mathrm{BTAH}]_{\mathrm{ads}}: \mathrm{Cu} \qquad (1)$$

where $[\mathrm{BTAH}]_{\mathrm{aq}}$ refers to BTAH dissolved in aqueous electrolyte and $[\mathrm{BTAH}]_{\mathrm{ads}}$: Cu refers to BTAH molecules adsorbed on the copper surface. Recent measurements [31] revealed that BTAH is attached to the copper surface via the triazole nitrogen in a vertical or tilted orientation. With this arrangement, the dipoles of the adsorbed BTAH molecules exercise lateral interaction effect with each other. An increase in $[\mathrm{BTAH}]_{\mathrm{aq}}$ shifts the above equilibrium toward the right giving a higher degree of surface coverage and hence imparting more protection.

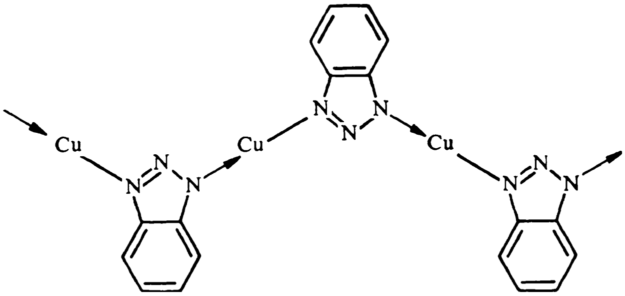
On the other hand, the second mechanism attributed the inhibition efficiency of BTAH to the formation of a protective film of Cu(I) BTA complex on the metal surface, i.e.,

$$\mathrm{Cu} + [\mathrm{BTAH}] = [\mathrm{Cu(I)BTA}] + \mathrm{H}^+ + \mathrm{e}^-, \quad \mathrm{pK_a} \sim 8.2 \qquad (2)$$

There is an ample evidence that the Cu(I) BTA complex exists in a polymeric form which further stabilizes the film, i.e.,

$$\mathrm{n(Cu(I)BTA)} = [\mathrm{Cu(I)BTA}]_{\mathrm{n}}. \qquad (3)$$

This polymeric chain has alternating copper atoms and BTAH molecules with the following proposed structure [32]:



The conditions under which either mechanism 1 or 2 prevails are the subject of some debate. The subject is attracting an increasing attention in efforts to elucidate the mechanism of inhibitive action [10, 11, 32–40]. Most of these studies were primarily concerned with the equilibrium properties of the protective film and its effects on the anodic and cathodic partial reactions. On the other hand, Youda et al. [10] have suggested that adsorption and complex formation are in equilibrium, i.e.,

$$n\mathrm{BTAH}_{ads.} + n\mathrm{Cu} = [\mathrm{Cu(I)BTA}]_n + n\mathrm{H}^+ + ne^-. \qquad (4)$$

Equation 4 reveals that increasing the pH value, the potential in the noble direction and the inhibitor concentration favor the formation of the protective polymeric complex, while adsorption becomes favorable in acidic media, at lower inhibitor concentration and when the potential changes to more negative values with the rate of adsorption of BTAH on a $\mathrm{Cu_2O}$ surface being faster than that on a CuO surface [12].

The inhibition efficiency of BTAH in a specific medium can be explained based on its chemical properties. Based on the pH of the medium, BTAH can exist in either one of three forms [11]. In strongly acidic media, BTAH can exist in a protonated form $\mathrm{BTAH_2}^+$, while in weakly acidic, neutral, and weakly alkaline media it has the form BTAH. On the other hand, in strongly alkaline media it is BTA^-. Considering that, Cu surface is positively charged in the solution it can easily be concluded which form is more and which is less favorable. Tromans [41] constructed the E–pH diagrams for systems containing Cu and BTAH that provide an indication of the type of species present under particular conditions, dependently on pH, potential, and inhibitor concentration. For detailed information about these diagrams and the theory behind them, see Ref. [41]. For example, it has been shown that the adsorption of BTAH on Cu surface is an exothermic process; therefore, it is obvious that any temperature increase will have an adverse effect on the inhibition efficiency [22, 26, 27]. From early times, it was frequently shown that the inhibiting efficiency of BTAH against the corrosion of copper increases with both immersion time and concentration in the electrolyte [13]. More recently, the kinetics of film growth were studied using quartz crystal microbalance [34, 40]. Hepel and Casteforis [40] showed that, the corrosion breakdown potential (the driving force needed to break the protective film) was very sensitive to the order of the formed monolayer where sometimes special treatment and a few hours of incubation were necessary to achieve the full protective efficiency of the film. For example, in case of a fresh Cu electrode immersed in BTAH solution, the observed low breakdown potential ($E_b = 20$ mV) could be substantially increased (up to $E_b = 800$ mV) after CV pretreatment with lower scan rates resulted in lower values of E_b. On the other hand, Al-Kharafi and co-workers [42] distinguished three regions in the time response of the microbalance upon injecting BTAH into the electrolyte. At short time of few minutes (1st region), a rapid linear growth of mass with time was observed which was attributed to the formation of a protective Cu(I)BTA complex. Few minutes later (2nd region), attachment of BTAH at a slower rate onto the inner Cu(I)BTA complex was observed. This was followed by a plateau (3rd region) indicating that the BTAH film attained an equilibrium mass and thickness, which increased with the concentration of BTAH. XPS examination showed that the intensity of the N1s peak increased with the time of immersion, indicating more BTAH on the surface. Based on these findings, Al-Kharafi and co-workers [42] suggested the formation of a duplex inhibitor film composed of an inner thin layer of Cu(I)BTA and an outer layer of physically adsorbed BTAH which increases in thickness with time and BTAH concentration. On the other hand, the quartz crystal immittance (QCI) technique was used to characterize the film acoustic resistance and the resonator parallel capacitance [40]. In acidic solutions, it was reported that the decrease in the maximum quartz resonator admittance associated with the increased resistance of the CuBTA film can be correlated with the reduced inhibition effectiveness of the formed protective film. In another study, bulk acoustic wave (BAW) technique was used to study the structure and real-time growth behavior of the Cu–BTA complex in sodium chloride solutions containing low concentration of benzotriazole [43]. It was shown that different growth kinetics of the film resulted in different inhibition abilities. With increasing BTAH concentration, the growth kinetics of the surface film changed from a parabolic law to a logarithmic law, CuO was found to disappear from the surface film which resulted in an increase in the inhibition efficiency. The critical concentration of BTAH was found to be 0.17 mM.

3 Inhibiting effects of benzotriazole, its derivatives, and blends

3.1 In clean environments

There are numerous investigations of the effect of BTAH on the corrosion of copper and its alloys in various environments such as chloride ions-containing electrolytes [44–48], nearly neutral solutions [22, 49], strongly acidic [29, 31, 50], and strongly alkaline media [21] and in atmosphere [51, 52]. Besides, it was shown that BTAH is the only inhibitor that provides effective protection of copper archeological artifacts during preservation process [49, 52]. For example, it was shown that BTAH can completely inhibit the corrosion of cupronickels in salt water [4, 18, 19, 53] as well as in acidic [37, 54, 55] environments. Based on enthalpy of adsorption calculations, these studies showed that the obtained values agreed very well with the value obtained for pure copper in the same media. Therefore, it was concluded that BTAH is a better inhibitor for copper than for nickel.

In another set of studies, BTAH was evaluated as corrosion inhibitor for brass alloys in different corrosive environments [14, 48, 56–63]. Sanad and co-workers [56] studied the effect of BTAH on the corrosion of brass alloys (90/10, 70/30, and 67/33 Cu–Zn) in 0.1 N HCl, 0.1 N H_2SO_4, and 0.1 N NH_4Cl by means of immersion tests and galvanostatic measurements. They found the inhibition efficiency of BTAH in 0.1 N HCl solutions to increase with increasing BTAH concentration. In contrast, the inhibition efficiency in 0.1 N H_2SO_4 was found to be inversely proportional to the BTAH concentration. They reported that the highest inhibition efficiency was obtained in the 0.1 N NH_4Cl electrolytes. They related the role of BTAH inhibition for brass corrosion to the chemisorption of BTAH molecules at some active sites on brass surfaces. They also found that the inhibition efficiency for 90/10 brass was greater than that for the 67/33 and 70/30 brasses. They believed that this might be because BTAH acts selectively as a copper complexing agent and left the exposed zinc relatively unaffected. On the other hand, de Costa and co-workers [63] studied the electrodissolution behavior of Cu and Cu–Zn alloys in 1 M HCl containing benzotriazole (BTA) using rotating ring-disk electrodes. They found that Cu(I) was the main product of Cu–Zn alloy dissolution with Cu(II) detected only at higher potentials. However, as the rest potential was approached, selective dissolution of Zn was increased. In the limiting current region, electrodissolution was under mass-transfer control with the rate of Cu component dissolution being equivalent to pure Cu dissolution with $CuCl_2^-$ as the diffusing species. Consequently, they proposed the possibility of the formation of a duplex film, a porous CuCl outer layer with a Cu(I)-BTA nonporous inner layer. In contrast, Mamas and co-workers [48] have investigated the corrosion inhibition of 70/30 brass alloy in 0.1 M NaCl using benzotriazole and showed that the addition of low concentration of benzotriazole (1.2×10^{-4} M) has enhanced the formation of ZnO and/or Zn-BTA films. On the other hand, Kosec and co-workers [57] studied the effect of BTAH on the corrosion of brass in 0.5 M NaCl. They reported the formation of mixed copper–zinc oxide polymer surface film (Cu_2O and ZnO oxides, and Cu(I)-BTA and Zn(II)-BTA polymers) that provided an effective barrier against corrosion of both metal components in the tested corrosive electrolyte. Antonijevic and co-workers [61] have investigated the corrosion behavior of Cu37Zn brass in a solution of sodium tetraborate (pH 10) with the addition of chloride ions and BTAH as an inhibitor. They found that chloride ions have a destroying effect on the surface of the Cu37Zn electrode in BTAH-free electrolytes while it showed much lesser destroying effect when the Cu-BTA polymer film was formed at its surface. Moreover, some other studies were devoted to evaluate BTAH as a corrosion inhibition of the stress corrosion cracking of brass alloys [14, 59, 62]. Shih and Tzou [62] used the slow strain rate technique (SSRT) to study the susceptibility of stress corrosion cracking (SCC) of 70/30 brass in fluoride solution ($pH = 6.2$) at 20 °C in the presence of BTAH. They found that the effective BTAH concentration was about 300 ppm or more in the presence of 1,000 ppm F^-, above which SCC could be effectively inhibited. On the other hand, the cathodic reaction on brass was found to be significantly polarized by the presence of BTAH. In another study [59] using same conditions, same authors showed that the addition of BTAH led to change in the cracking type from intergranular to ductile fracture. On the other hand, Sayed and co-workers [14] have investigated the effect of BTAH on the SCC corrosion of α-brass in 0.1 M $NaNO_2$ solutions. They found the maximum stress and the time to failure to be increased with the increase in BTAH concentration. The mode of cracking changed from transgranular, in nitrite solution alone or in the presence of low concentrations of BTAH, to ductile failure at higher concentrations of BTAH.

The corrosion of bronzes has also been investigated in the presence of BTAH [15, 60, 64]. Walker [64] studied the oxidation behavior of tin bronze pretreated with benzotriazole. The study showed that prior dipping of bronze into a solution of BTAH has reduced the rate of oxidation of the material in air over the temperature range 350–550 °C. However, the copper–benzotriazole complex was found to be evaporated from the dipped bronze surface at about 230 °C with an exothermic reaction. On the other hand, the inhibiting effect of BTAH on the corrosion of α-Al-bronze (Cu–7% Al) in 3.4% NaCl was studied by Ashour and co-workers [15]. They showed that BTAH had a stronger inhibiting effect on the anodic dissolution of copper than on the cathodic reduction of oxygen. It was also shown that the interaction of BTAH with a Cu_2O-covered alloy surface is faster than on reduced alloy surfaces, although the protection efficiency on the latter was slightly better than on the former. Hassairi and co-workers [60] investigated the behavior of an archaeological bronze in the presence of BTAH in 0.1 M NaOH. They showed that the presence of 15 mmol/L of BTAH in distilled water at $pH = 9$ resulted in a maximum protection efficiency of 64 ± 3% over 30 min to 96 h of immersion. However, the use of pre-polarized electrode resulted in a maximum efficiency of 97.4% after 96 h of immersion time.

Although BTAH was shown to be very effective in near neutral and slightly alkaline media, its effect is weaker in highly acidic and highly alkaline media as well as in media containing aggressive ions. Therefore, the investigation of the effect of BTAH derivatives came into play.

The behavior of BTAH derivatives was reported to be quite similar to that of BTAH. The introduction of substituent groups has no effect on the inhibition mechanism while it has an influence on the inhibition efficiency [22, 23, 25, 28, 29, 65]. Arancibia and co-workers [28] studied the effect of BTAH and its derivatives (5-methyl-BTAH and 5-chloro-BTAH) on the corrosion of copper in aerated 0.1 M HCl solution. They found that BTAH and 5-methyl-BTAH acted as cathodic inhibitors through the adsorption of $BTAH_2^+$ on Cu. On the other hand, the effect of 5-chloro-BTAH was shown to depend on its concentration being of mixed anodic/cathodic mode at low and moderate concentrations while it acts as an anodic inhibitor at high concentration associated with passivation and CuBTA formation. The presence of chlorine in the 5-position enables the formation of the partially protonated species of BTAH while nitrogen is still responsible for bonding with Cu surface. In another study, Frignani and co-workers examined the effect of 5-methyl-BTA, 5-butyl-BTA, 5-hexyl-BTA and 5-dodecyl-BTA on the corrosion of copper in 3.5% NaCl ($pH = 7$ and 2.5) and 0.1 M $NaClO_4$ ($pH = 7$) [66, 67]. They concluded that the tested compounds produce films that were able to inhibit the oxygen reduction process depending on the alkyl chain length, but only 5-hexyl-BTA film succeeded in hindering the copper oxidation reaction, even in acidic NaCl. They related the protective effect of 5-hexyl-BTA to the hydrophobic effect of the alkyl chain, rather than to an electron releasing inductive stabilization effect. Generally, it is noticed that the interaction between inhibitor and metal surface enhances with substituents in 5-position of the inhibitor molecule. In contrast, the substitution in the 1-position of BTAH was found to have no effect on improving its inhibition capability. Alego [68] and co-workers have found l-[N,N-bis-(hydroxyethyl)aminomethyl]-benzotriazole (BTLY) to be ineffective in preventing dezincification of brass in H_2SO_4 electrolyte with the obtained efficiency being comparable to that observed for BTAH under the same conditions.

The existence of a synergistic inhibiting effect between BTAH and iodide ions on the corrosion of copper in H_2SO_4 electrolyte was first reported by Wu and co-workers [69].

The synergistic effect is assumed to be a result of initial contact adsorption of iodide anions on Cu that facilitates the adsorption of protonated BTAH on the Cu surface [50] or due to the formation of Cu(IBTA) complex polymer film [69]. Villamil and co-workers [30] also noticed a synergistic effect between BTAH and sodium dodecyl sulfate (SDS) on the inhibition of copper corrosion in sulfuric acid solution. Therefore, synergism has become one of the most important effects in the inhibition processes and it serves as the basis for all modern corrosion inhibitor formulations. Ashour and co-workers [17] investigated the effect of blending BTAH and Thiourea (TU) on the anodic dissolution of copper at pH = 1.8. They found that this blend can exert either synergistic or antagonistic effects depending on their relative concentrations in the blend. Synergism was only observed in blends containing higher, i.e., $\geq 10^{-2}$ M, concentration of TU. The antagonistic effects of TU were discussed in the light of its tendency to produce H_2S which promotes the anodic dissolution of copper. Analysis of the desorption behavior of the individual compounds using the Langmuir isotherm revealed stronger interaction of the copper surface with BTAH than with TU, as judged by free energy of adsorption values of −18.8 and −8.7 kJ/mol for BTAH and TU, respectively. A large number of similar measurements were performed using blends containing various concentrations of BTAH and TU, the results obtained being summarized in Table 1.

Table 1 Inhibition Efficiency (θ) of Blends Containing Various Concentrations of Benzotriazole (BTAH) and Thiourea (TU) on the Anodic Dissolution of Copper [17]

Composition of blend		θ	Interaction
BTAH (M)	TU		
5×10^{-5} (0.56)	–	–	
1×10^{-4} (0.72)	1×10^{-2} (0.90)	0.89	None
1×10^{-3} (0.96)	1×10^{-3} (0.72)	0.99	Slight synergism
1×10^{-3} (0.96)	1×10^{-2} (0.90)	0.91	Slight antagonism
1×10^{-3} (0.96)	5×10^{-2} (0.52)	0.69	Moderate antagonism
1×10^{-3} (0.96)	1×10^{-1} (0.15)	0.23	Strong antagonism
5×10^{-3} (0.99)	1×10^{-1} (0.15)	0.80	Moderate antagonism
1×10^{-2} (0.997)	1×10^{-4} (0.42)	0.99	None
1×10^{-2} (0.997)	1×10^{-3} (0.72)	0.99	None

The numbers in parentheses donate the protection efficiency

Note that, the values in parentheses refer to the protection efficiency (degree of coverage) of the individual additives at a particular concentration. The data listed in Table 1 show the conditions under which synergism, antagonism or no interaction occurred between BTAH and TU. Synergism is indicated by a value of θ (blend) greater than either θ_{BTAH} or θ_{TU}. On the other hand, antagonism occurred when θ (blend) was less than the greater of the two values for θ_{BTAH} or θ_{TU}. Inspection of Table 1 reveals the following:

At low concentrations of one inhibitor, e.g. 10^{-4} M, the efficiency of the blend was equal to that of the second inhibitor when no interaction occurred between the inhibitors.

At moderate concentration values in the blend, e.g., 10^{-3} M BTAH + 10^{-3} M TU, slight synergism occurred.

At high concentrations of TU, i.e., ≥ 0.05 M had a detrimental effect on the concentration of TU.

However, for a given concentration of TU, an increase in the concentration of BTAH increased the protection efficiency. This indicates that higher concentrations of BTAH reduced the detrimental effect of TU.

3.2 In sulfide-polluted environments

The systematic study of the problem of the sulfide pollution on the efficiency of benzotriazole on inhibiting the corrosion of copper and its alloys started in middle of the twentieth century. At the end of twentieth century, there is still no general agreement about the mechanisms involved in the process. There is a large number of variables, e.g., composition of the material, concentration of pollutants, environments… etc. In spite of the high corrosion resistance of these alloys, they suffered from severe corrosion in media polluted by sulfide ions [18, 20, 69–84]. This is a problem of considerable significance in view of the fact that many industrial water streams and indeed some natural water bodies are polluted by dissolved sulfides. It is documented that the corrosion rate of Cu-base alloys increases by a factor of 10–30 when seawater contains sulfur compounds as impurities [85].

It is now becoming broadly realized that copper and its alloys face service environments polluted by sulfide ions. This raises a question as to whether BTAH retains its high inhibiting efficiency against the corrosion of Cu alloys in such media. Furthermore, it poses a question as to whether BTAH and sulfide ions compete with each other on the adsorption on the substrate surface. This point has implications on the behavior of copper and its alloys in electrolytes containing both BTAH and sulfide ions. The recent work of Al-Farawati and co-workers [86] showed the possibility that Cu can be complexed by both sulfide and complexing agents in solution containing both species. Furthermore, Christensen and co-workers [87] showed that BTAH was least stable in sulfur-containing environments disappearing from the surface even at room temperature. However, in oxygen-containing environments, they showed that BTAH was quickly lost from the surface at temperatures above 150 °C. On the other hand, in inert atmospheres such as pure nitrogen and in vacuum, BTAH was shown to be quite stable up to temperatures near 280 °C. These findings suggest that the loss mechanism involved a chemical reaction rather than solely a thermal process. In such environments, these metallic components serve in media that are inhibited by BTAH and polluted by corrosion promoters. Such pollutants can adsorb on the metal surface and interfere with reactions 1 and 2 (above) and alter the corrosion mechanism and the efficiency of the inhibitor.

To this end, Al-Kharafi and co-workers [76] showed that the injection of sulfide ions into a benzotriazole inhibited salt water damages the protective Cu(I)BTA film very rapidly, increases the corrosion rate and leads to the formation of copper sulfide. This effect is quite marked at a sulfide concentration as low as 10^{-5} M (about 0.3 ppm sulfur) in the presence of 10^{-2} M BTAH, which is 1,000-fold greater than that of the sulfide ions. The intensity of sulfide attack increases with its concentration. Prolonged pre-passivation of copper in the BTAH protected medium even at high concentration does not markedly improve the resistance of the protective film to sulfide attack. This finding is contrary to the well-documented phenomenon in unpolluted media where the inhibiting efficiency of BTAH increases with the time of immersion and the concentration of the inhibitor. X-ray photoelectron spectroscopy (XPS) revealed the presence of both sulfide and BTAH on the corroded surface indicating that sulfide attack is localized [76].

Same authors showed also that the electrochemical impedance of Cu in benzotriazole inhibited media (0.5 M Na_2SO_4 + 0.05 M H_2SO_4) was affected by the addition of sulfides [70]. This caused an order of magnitude decrease in the polarization resistance and an increase in the double layer capacity. The appearance of sulfur peaks in X-ray photoelectron spectroscopy (XPS) spectra of the sulfide treated surfaces was accompanied by a significant of increase in the atom percent of Cu and a significant decrease in the atom percent of N and of C (and hence, of BTAH) in the surface layer. The results were explained on the basis of the ability of the sulfides to break down the protective BTA film and be adsorbed on the copper surface to catalyze its corrosion. The XPS spectra suggested the formation of copper sulfides. The parameters calculated from the measured EIS diagrams obtained under various conditions [83] are comparable to those obtained using more complex equivalent circuits [9, 13, 35, 88]. The mean atom concentrations in the surface layer were also determined from the areas of the respective peaks under various conditions.

XPS showed that the incorporation of sulfur (S 2p) on the surface layer is accompanied by a significant decrease in the amount of BTAH on the surface, as judged from the decrease in the atom percent of N 1s and the C 1s signals. The XPS spectra point to the formation of copper sulfides upon addition of the sulfide species to the BTAH inhibited media [83].

On the other hand, some studies were devoted to investigate the effect of sulfide pollution on the performance of Cu alloys in BTAH-containing electrolytes. It was shown that the addition of sulfide ions to a solution of 0.58 M NaCl containing benzotriazole results in a decease of the inhibiting efficiency of BTAH and a momentary increase of the dissolution rate of α-brass at potentials above the corrosion potential [82]. The effect depends on the sulfide ion concentration and the potential selected for testing. The results were explained by the possibility of the decomposition of the protective Cu(I)BTA film, caused by the extraction of Cu(I) ions from the film and formation of Cu_2S [82]:

$$n\mathrm{S}^{2-} + 2[\mathrm{Cu(I)BTA}]_n \rightarrow n\mathrm{Cu_2S} + 2n\mathrm{BTA}^-. \tag{5}$$

The breakdown of the film allows metal dissolution from the underneath surface and further promotes the effects of sulfide ions [82]. This hypothesis can be realized based on the high stability of Cu_2S (stability constant of 4×10^{47} [89]). The formation of the Cu(I)BTA complex in chloride-containing electrolytes is commonly represented by an equilibrium of the form [41, 90, 91]:

$$\mathrm{CuCl_2^-} + \mathrm{BTAH} \leftrightarrow \mathrm{Cu(I)BTA} + \mathrm{H^+} + 2\mathrm{Cl^-}. \tag{6}$$

A value of 1.54×10^{-2} has been reported [89] for the stability constant for the Cu(I)BTA complex $K_{Cu(I)BTA}$ in 1 M NaCl solution of pH 3 i.e.:

$$K_{\mathrm{Cu(I)BTA}} = \frac{[\mathrm{H^+}][\mathrm{Cl^-}]^2[\mathrm{Cu(I)BTA}]}{[\mathrm{CuCl_2^-}][\mathrm{BTAH}]}. \tag{7}$$

Since the BTAH molecules participating in complex formation might be adsorbed on the metal surface or coming directly from the diffusion layer, the integrity of this film and hence its protection efficiency will depend on the conditions of its growth. It is now becoming increasingly clear that sulfide ions affect the tendency and rate of corrosion of many copper base alloys [72, 74, 78, 79, 92], which are often protected against corrosion using BTAH. In view of the great difference between the stability constants of Cu_2S and the Cu(I)BTA complex (4×10^{47} and 1.54×10^{-2}, respectively) sulfide ions can extract the Cu(I) ions from the Cu(I)BTA complex, i.e., (see reaction 4). For example, the obtained values of inhibition efficiency for α-brass corroded in 0.58 M NaCl in the presence of both BTAH and sulfide ions are presented in Table 2.

As for cupronickels, the interaction of BTAH with the surface of a corroding Cu10Ni alloy in sulfide-free and sulfide-polluted salt solutions was well documented by Allam and co-workers [18–20]. Concentrations of BTAH

$\geq 5 \times 10^{-4}$ M were shown to inhibit the corrosion of Cu10Ni alloy in both the polluted and the unpolluted media. This finding was substantiated by measurements of mass loss, current transients and examination of the surface by SEM microscopy. Results are shown in Table 3 and Fig. 1a, b for clean and polluted electrolytes, respectively [18].

The above results implied that the presence of sulfide ions (at 2 ppm) decreases the inhibiting efficiency of BTAH against the corrosion of Cu10Ni alloy. The results were interpreted in terms of competitive adsorption of the protective BTAH and the corrosion promoting sulfide ions on the alloy surface. In the presence of high concentration of BTAH, X-ray diffraction measurements revealed the absence of copper sulfide in the corrosion product film [18] with metallographic examination revealed a much lower extent of corrosion [19].

Some other studies were devoted to copper–nickel alloys with the interest has been focused mainly on the role of iron, added either as ferrous sulfate or as an alloying element, in the formation of a protective layer of hydrated ferric oxide that protects the metal against corrosion [93, 94]. The nature of the protective film formed by benzotriazole (BTAH) on the surface of the Cu10Ni alloy in deaerated 0.5 mol L^{-1} H_2SO_4 solution containing Fe(III) ions as oxidant was investigated by weight-loss, calorimetric measurements, and by surface-enhanced Raman spectroscopy (SERS). The SERS measurements showed the protective film to be composed of the $[Cu(I)BTA]_n$ polymeric complex as well as the adsorption of BTAH molecules on the electrode surface. A modification of the BET isotherm for adsorption of gases in solids was proposed to describe the experimental results obtained from weight-loss experiments that suggested an adsorption in multilayers. On the other hand, the electrochemical studies of pure copper and pure nickel in 0.5 mol L^{-1} H_2SO_4 in the presence and in the absence of BTAH have also been made as an aid to interpret the results. The calculated adsorption free energy of the cuprous benzotriazole on the surface of the alloy was found to be in accordance with the value for pure copper [95].

4 Adverse effect of benzotriazole

It is shown elsewhere [84] that sulfide ion imparted a damaging effect on the remarkable inhibiting efficiency of benzotriazole against the corrosion of copper in salt water. In fact, under some conditions, sulfide ions not only

Table 2 Effects of sulfide ions (at 1.25×10^{-4} M) and/or BTAH (at 10^{-2} M) on the corrosion rate and corrosion potential of alpha brass in 0.58 M NaCl [68]

Electrolyte	I_{corr}, mA cm^{-2}	E_{corr}, mV_{NHE}	Protection efficiency, %P
0.58 M NaCl	0.85	+40	–
0.58 M NaCl + 10^{-2} M BTAH	0.02	+43	98
0.58 M NaCl + 10^{-2} M BTAH + 1.25×10^{-4} M S^{2-}	0.40	−20	53

Table 3 Variation of the protection efficiency (% P) with the BTAH concentrations after immersion for 5 h in both unpolluted and polluted media [18]

[BTAH], M	10^{-4}	5×10^{-4}	10^{-3}	5×10^{-3}	10^{-2}	2×10^{-2}
(% P) 3.4% NaCl	68	86	100	100	100	100
(% P) 3.4% NaCl + 2 ppm S^{2-}	–	42	80	82	89	95

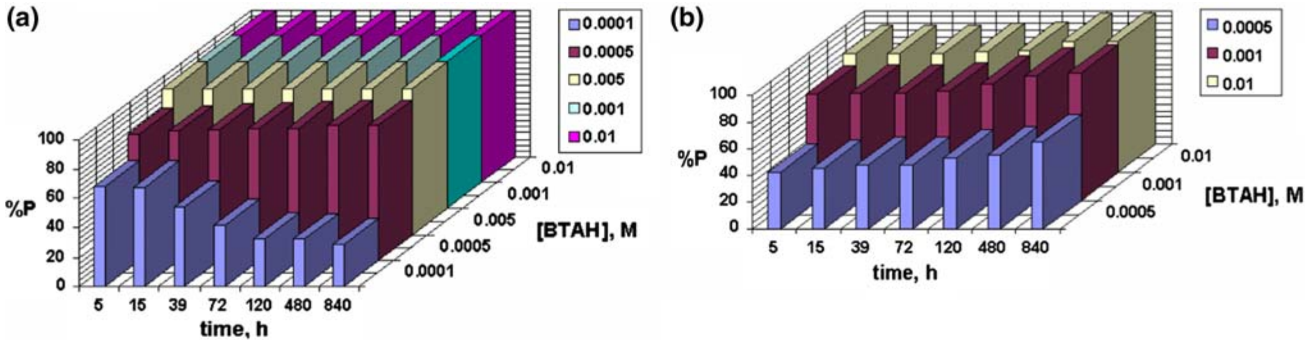


Fig. 1 3D plot for the inhibition efficiency of BTAH for Cu10Ni alloy corroded in (**a**) 3.4% NaCl and (**b**) 3.4% NaCl + 2 ppm S^{2-} [18]

eliminate the inhibiting effects of BTAH, but also promote the corrosion reaction to a greater extent than in absence of BTAH. This suggested the existence of a form of interaction between HS^- ions and BTAH. The loss of efficiency of BTAH under the effect of HS^- ions was rationalized on the basis of competition between HS^- ions and BTAH for adsorption on the copper surface and for complex formation with copper ions. A similar finding was reported by Fiaud and Ghimouz [96] who studied the effect of hydrogen sulfide on the atmospheric corrosion of copper preconditioned in BTAH. Same authors have also shown a remarkable promoting effect of water vapor on the rate of growth of Cu_2S on copper which was preconditioned in BTAH. Recently, Allam and Ashour reported a promoting effect of BTAH (at concentrations $\leq 10^{-4}$ M) on the corrosion of Cu10Ni alloy in sulfide polluted salt water [20]. The change in the role of BTAH from a corrosion inhibitor (at 5×10^{-4} M) to a corrosion promoter (at 10^{-4} M) in the polluted medium was confirmed using mass loss, current transients and potentiostatic polarization measurements as well as examining the corroded surfaces using optical and SEM microscopy [19, 20]. The results of the performed potentiostatic polarization are shown in Table 4:

Table 4 implies that BTAH shifts the free corrosion potential in the noble direction (from −60 mV to +40 mV) indicating that it acts as an anodic inhibitor. Note that the corrosion current in the presence of 10^{-4} M BTAH (5.23×10^{-4} mA/cm^2) is greater than that in the blank electrolyte (3.02×10^{-4} mA/cm^2). This finding adds to the evidence that insufficient levels of anodic inhibitors promote localized corrosion [97, 98].

It appears that 10^{-4} M BTAH was not sufficient to cover the whole surface, i.e., it covers only a small part of the anodic sites while the cathodic sites are still active. Therefore, alloy dissolution increases with time. A similar phenomenon was observed by Walker [3] who found that BTAH promoted the corrosion of Cu in a medium containing ammonium hydroxide and ferric chloride.

5 Conclusions

The chemistry of Benzotriazole (BTAH) was reviewed which was shown to be the crucial element in determining the inhibition ability of BTAH. The two mechanisms for the inhibition of BTAH to the corrosion of Cu and Cu alloys were summarized. BTAH was found to be an excellent inhibitor for the corrosion of Cu and its alloys in clean environments. However, the presence of pollutants such has sulfide ions showed a damaging effect on the remarkable inhibiting efficiency of benzotriazole against the corrosion of Cu and its alloys. Under some conditions, sulfide ions not only eliminate the inhibiting effects of BTAH but also promote the corrosion reaction to a greater extent than in the absence of BTAH. The use of BTAH derivatives was shown to increase the inhibition efficiency but not the mechanistic action. On the other hand, the use BTAH blends was reported to be a great alternative in case of aggressive environments.

Table 4 Effect of different concentrations of BTAH on the corrosion current and corrosion potential of Cu10Ni alloy in 3.4% NaCl + 2 ppm S^{2-}[20]

Electrolyte	E_{corr}, mV_{NHE}	I_{corr}, mA cm^{-2}
3.4% NaCl + 2 ppm S^{2-} (blank)	−60	3.02×10^{-4}
Blank + 10^{-4} M BTAH	+40	5.23×10^{-4}
Blank + 5×10^{-4} M BTAH	+40	1.27×10^{-4}

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