

Photo-Corrosion of Different Metals during Long-Term Exposure to Ultraviolet Light

T.D. Burleigh,^{†,*} C. Ruhe,^{**} and J. Forsyth^{*}

ABSTRACT

The effect of ultraviolet light on the corrosion rates of different metals was studied in two separate investigations. Metal samples were immersed in a flowing fresh water discharge stream for either three or five months under both ultraviolet (UV) light and dark conditions. Weight-loss results demonstrated that pure zinc, carbon steel, aluminum 6061 (UNS A96061), pure copper, and pure silver all experienced photo-corrosion, that is, a greater weight loss under exposure to UV light vs in the dark. Titanium, zirconium, Type 304 (UNS S30400) stainless steel, and pure nickel showed a weight gain during immersion, but the cause of the weight gain was uncertain. Pure nickel and Al 5052 (UNS A95052) did not show any reproducible trend. Zirconium, titanium, and brass showed a photo-effect in one investigation, but not in the other. The photo-corrosion is explained with models based on the photo-voltages measured on corroded metal samples.

KEY WORDS: *n-type, p-type, photo-corrosion, photo-inhibition, photo-voltage, pitting, ultraviolet light*

INTRODUCTION

It has been reported in the literature that the passive oxide films on metals are semiconductors and that

these passive films exhibit photo-effects such as photo-currents and photo-voltages in the presence of light.¹⁻³ Some researchers have reported photo-inhibition and photo-corrosion for different metals exposed to ultraviolet (UV) light under laboratory conditions.⁴⁻¹² Lenhart, et al., reported that white light inhibited the pitting of nickel in a buffered chloride solution.⁴ Schmucki and Bohni reported on the UV photo-inhibition of corrosion of iron immersed in a borate buffer solution.⁵ MacDonald and coworkers reported on the photo-inhibition of pitting corrosion of Type 304 (UNS S30400)⁽¹⁾ stainless steel (SS) in chloride solutions.⁶⁻⁷ Kalinauska, et al., reported on the photo-corrosion of zinc in chloride solutions.¹¹

The question is, are these photo-effects simply interesting laboratory artifacts, or is there a significant change in the corrosion rate of the metal? This paper describes the results of two separate field tests of photo-corrosion of metals in flowing fresh water.

EXPERIMENTAL PROCEDURES

The results herein are from two separate investigations, the first by Ruhe and Burleigh in 1997-1998,¹³ with nine different metals tested (Table 1) and the second investigation by Forsyth and Burleigh in 1999-2000,¹⁴ with ten different metals tested (Table 2). In each investigation, the metal samples were immersed in the discharge stream of the Franklin Regional Municipal Sanitary Authority (FTMSA) where UV light (Trojan System UV3000^{†,15}) was used to disinfect the treated water before it was discharged into Turtle Creek. The average discharge rate was

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⁽¹⁾ UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.

[†] Trade name.

TABLE 1
Sheet Metal Samples Exposed for 3 Months by Ruhe during 1997-1998

Material	Composition (wt%)	UNS
Zr 702	Max. 4.5Hf-0.005H-0.025N-0.05C-0.16O-0.20Fe+Cr-balance Zr	R60702
Ti Grade 2	Max. 0.03N-0.1C-0.015H-0.3Fe-0.25O-balance Ti	R50400
Type 304 SS	18Cr-8-Ni-0.31Mo-0.055C-0.18Mn-balance Fe	S30400
Ni 99.5	99.5% Ni	—
Al 5052	2.35Mg-0.28Cr-<0.05Si,Ni, Cu, Mn, or Zn-balance Al	A95052
Cu 99.9	99.9% Cu	—
Cu-Zn	Brass, 70Cu-30Zn	C26000
Low C-Steel ASTM A366	0.19Mn-0.18Cr-0.037C-0.033Al-0.023P<0.10Ni or Si-<0.05Mo-0.01S-balance Fe	G10050
Zn 99.9	99.9% Zn	Z15001

TABLE 2
Sheet Metal Samples Exposed for 5 Months by Forsyth during 1999-2000

Material	Composition (wt%)	UNS
Zr 702	Max. 4.5Hf-0.005H-0.025N-0.05C-0.16O-0.20Fe+Cr-balance Zr	R60702
Ti Grade 2	Max. 0.03N-0.1C-0.015H-0.3Fe-0.25O-balance Ti	R50400
Type 304 SS	18Cr-8-Ni-0.31Mo-0.055C-0.18Mn-balance Fe	S30400
Ni 99.5	99.5% Ni	—
Ag 99.9	99.9% Ag	—
Al 6061-T6	1.0Mg-0.6Si-0.2Cu-0.2Cr-balance Al (approximate)	A96061
Cu 99.9	99.9% Cu	—
Cu-Zn	Brass, 70Cu-30Zn	C26000
C-Steel ASTM A366	0.19Mn-0.18Cr-0.037C-0.033Al-0.023P<0.10Ni or Si-<0.05Mo-0.01S-balance Fe	G10050
Zn 99.9	99.9% Zn	Z15001

2.5 million gallons of water per day (8 m³/min). The UV system consisted of 112 parallel, 27-W, 58-in.-length, fluorescent UV lamps. One set of duplicate metal samples was placed in the discharge stream in the midst of the UV lamps, while the second set of duplicate metal samples was placed upstream and experienced only the normal day/night cycles ("dark"). The dark Ruhe samples were ~2 m below the water level while the other samples were immersed in 0.3 m to 0.5 m of water. Once every week or two, the disinfection channel was drained for 1 h to 2 h for rinsing.

Four sheet samples of each metal were cut to 2.5 cm by 5.0 cm, polished to 600-grit silicon carbide (SiC), weighed, and then mounted on acrylic racks with nylon bolts. Duplicate samples were exposed in the dark and duplicate samples were exposed in the UV light. The sample surface area was ~23 cm², after subtracting the area shielded by the nylon bolts. The Forsyth tests used Apiezon, Type L¹ vacuum grease under the nylon bolts and nuts to prevent the crevice corrosion that ruined the steel samples in the previous Ruhe tests. At the end of 3 months, the samples were removed and rinsed, then cleaned with a soft bristle brush with warm soapy water, and then dried and weighed. The Forsyth samples were removed after 3 months, cleaned and weighed, and then re-immersed for 2 more months, for a total of 5 months, then cleaned and weighed a second time. The Forsyth results are the 5-month results, with the

exception of the pure copper, which is a 3-month result. (The copper samples appeared to have been switched on the second immersion.) All tests were conducted during the winter months so the water temperature was ~10°C. The discharge water had a neutral pH (pH = 6.8 to 7.4) with typical water concentrations of 125 ppm Cl and 62 ppm SO₄.

Simultaneous with the field tests, laboratory tests were conducted in municipal Pittsburgh water for comparison. The laboratory metal samples were corroded for several weeks in stirred municipal water that was open to the air and exposed only to darkness or room lights. The open-circuit potential of the laboratory-corroded samples was measured in the dark, then under illumination with a 150-W xenon arc lamp. The reported photo-voltage was the change in the potential between the "dark" conditions and the UV conditions. Linear polarizations were also conducted under UV and dark conditions with and without Schott-colored glass filters, but these results were too scattered for confident interpretation. In future work it would be better to measure the photo-voltages on a monthly basis directly on the metal samples that were exposed in the discharge stream.

RESULTS AND DISCUSSION

FTMSA Field Results

The results from the 3-month immersion by Ruhe are shown in Figure 1. The zinc, steel, and alu-

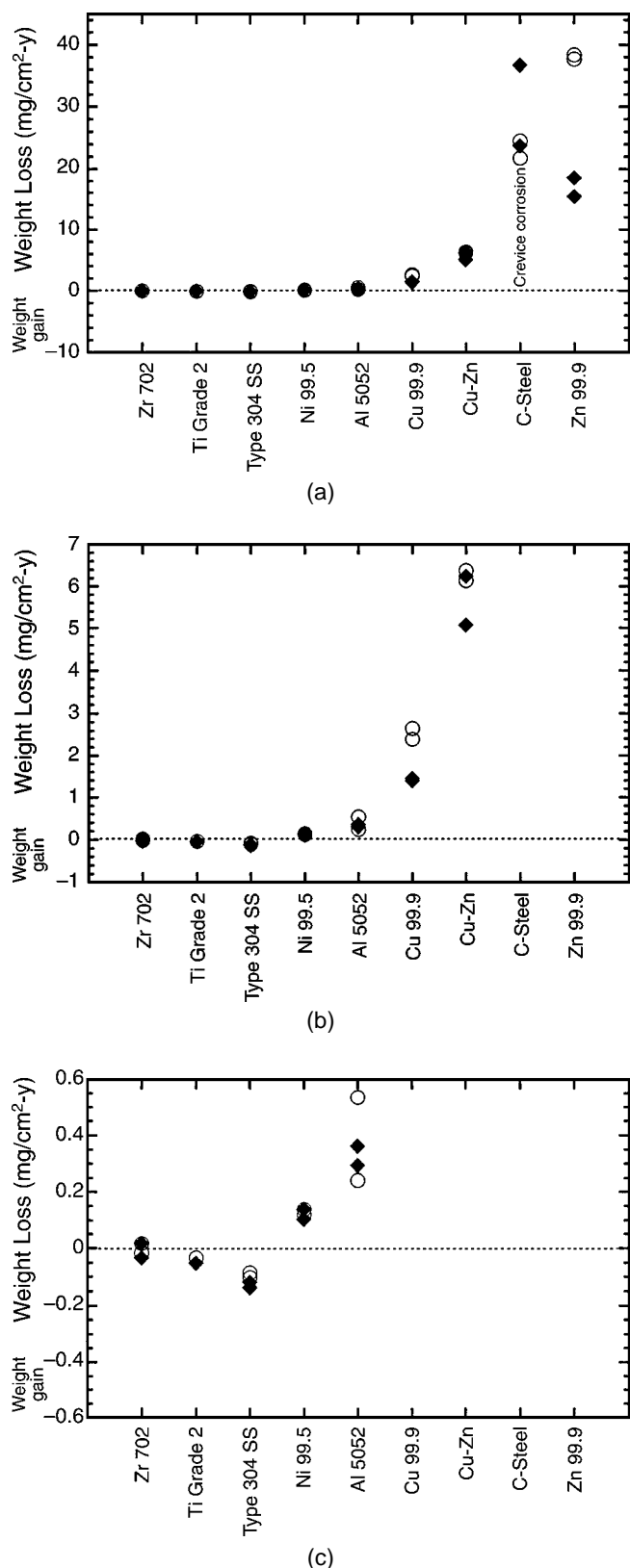


FIGURE 1. Weight loss under UV exposure is shown with the open circles, while weight loss in the dark is shown with the dark diamonds. Graphs a, b, and c are the same data, but with increasing y-axis scale. The Ruhe investigation found photo-corrosion of (a) zinc and (b) copper.

minum corroded by pitting corrosion, while the brass and copper corroded by uniform corrosion. In Figure 1(a), the pure zinc showed twice the weight loss under exposure to the UV light vs the dark. The steel sample also experienced crevice corrosion, which ruined any trends. In Figure 1(b), the copper showed 75% greater weight loss under the UV light. In Figure 1(c), the titanium and Type 304 SS showed weight gain during the immersion, with 50% less weight gain under the UV light vs the dark. The other metals (zirconium, nickel, Al 5052 [UNS A95052], and brass 70-30) showed no consistent trend.

The results from the 5-month immersion by Forsyth are shown in Figure 2 (the copper data is the 3-month immersion). In Figures 2(a) and (b), the zinc, carbon steel, Al 6061, pure copper, and pure silver all showed greater weight loss under UV exposure vs the dark. In this investigation, the brass exhibited a slight photo-inhibition of corrosion, with the samples in the light showing slightly less weight loss. The zinc, aluminum, and steel corroded by pitting corrosion, while the copper and the silver corroded by uniform dissolution. The zirconium, titanium, Type 304 SS, nickel, and the dark silver all showed weight gain. The silver exposed to the UV light became completely black (silver sulfide Ag_2S), while in the dark the silver maintained a silver surface. The black layer was washed from the UV silver with the warm soapy water, resulting in a weight loss. However, in the dark, the washed silver had a weight gain. In this second investigation, the nickel and the titanium showed no consistent trend in weight gain with or without light.

The cause of the weight gain is uncertain. Thickening of the passive film alone could not account for the entire weight gain. The authors postulate some type of deposit on the surface, such as 0.5 micron of calcium carbonate ($CaCO_3$). The zirconium showed an increased weight gain in the UV suggesting that there was photo-induced deposition. Notably, the Type 304 SS again showed less weight gain in the UV, suggesting a photo-inhibition of deposition. Unfortunately, no surface analysis was conducted on the corroded samples so the composition of the deposits is unknown.

Laboratory Results

Several tests were conducted in the laboratory, but the most consistent results were the photo-voltages measured by Forsyth (Figure 3). These photo-voltages were measured on the laboratory-corroded samples and not on the field samples. Tests with the Schott color glass filters demonstrated that the photo-effect was caused by visible and UV light (band-gap transitions) and not a result of infrared light (heating). When the corroded zinc, Al 6061, and nickel samples were exposed to UV light, the open-circuit potential (OCP) jumped to more noble voltages

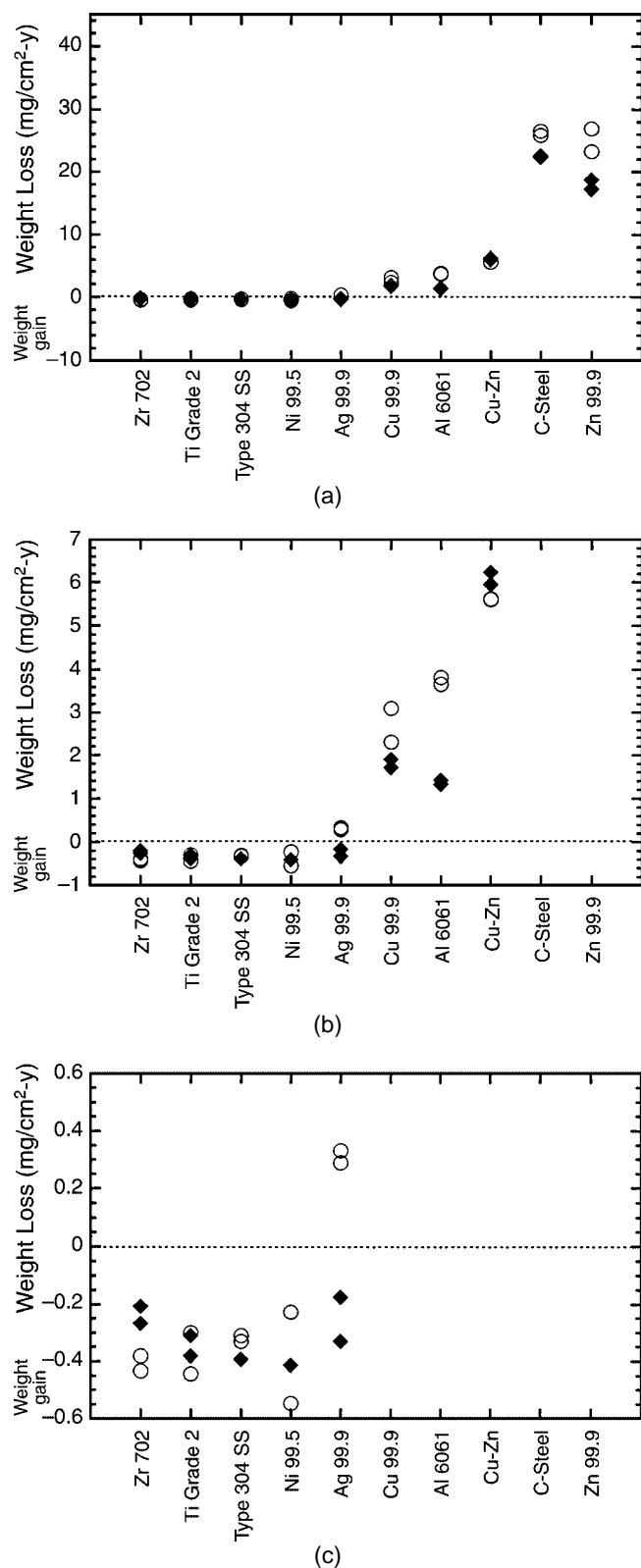


FIGURE 2. Weight loss under UV exposure is shown with the open circles, while weight loss in the dark is shown with the dark diamonds. Graphs a, b, and c are the same data, but with an increasing y-axis scale. The Forsyth investigation demonstrated photo-corrosion of (a) zinc and steel, (b) Al 6061 and copper, (c) and silver. The brass (Cu-Zn) showed a slight inhibition of corrosion.

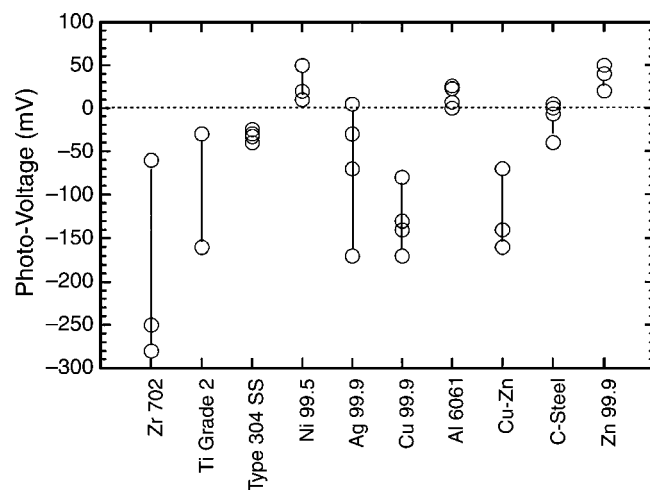


FIGURE 3. Photovoltages for different metals under illumination by white light. The photo-voltage is the change in the open-circuit potential for a corroded metal sample between the dark and exposure to the focused light of a 150-W xenon arc lamp. Nickel, Al 6061, and zinc all show a positive photo-voltage, while the other metals show a negative photo-voltage.

(positive photo-voltages). When the corroded brass, copper, silver, stainless, titanium, and zirconium were exposed to UV light, the OCP dropped to more active voltages (negative photo-voltages).

The proposed explanation for these photo-voltages is shown in the band models in Figures 4 and 5 (based on Gerischer¹⁶). The UV photons can create hole-electron pairs in the oxide film. If the conduction and valence bands are bent upward at the water interface (Figure 4), then the electrons can flow to the metal giving it a negative charge (negative photo-voltage). The holes will flow in the opposite direction, toward the water interface, causing dissolution of the metal oxide due to the missing shared electron (Gerischer¹⁷). Figure 4 illustrates this dissolution model in which the light can cause uniform corrosion of metals with a negative photo-voltage.

On the other hand, if the valence and conduction bands are bent downward as shown in Figure 5, then the positive holes will flow to the metal giving it a positive charge (positive photo-voltage). The electrons will flow in the opposite direction to the water interface, accelerating the cathodic reaction, which is either hydrogen evolution or oxygen reduction. If the cathodic reaction is accelerated, then pitting corrosion can also be accelerated, leading to increased weight loss. Figure 6 illustrates the pitting model for the case where light causes a positive photo-voltage and accelerates pitting corrosion. In summary, under UV illumination, the metals with a positive photo-voltage (Al and Zn) can experience increased pitting corrosion (Figure 6), while metals with a negative photo-voltage (Zr, Ag, and Cu) can experience increased uniform corrosion (Figure 5).

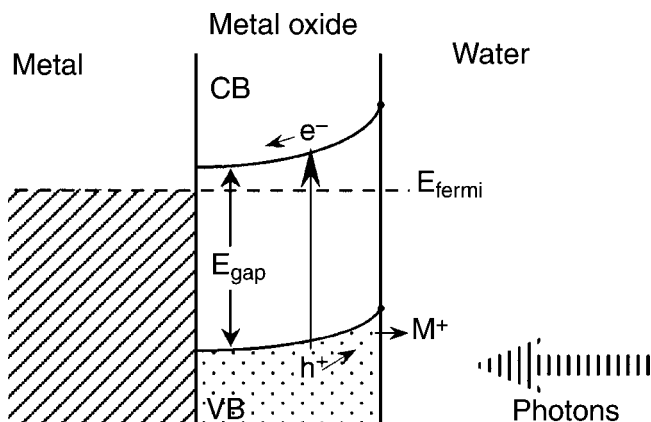


FIGURE 4. If the oxide energy bands are bent downward to the metal, illumination with UV light causes electrons in the surface oxide to flow to the inner metal, which gives a negative photo-voltage. The positive holes flow to the electrolyte interface where they accelerate dissolution or oxide thickening due to the missing valence electrons.

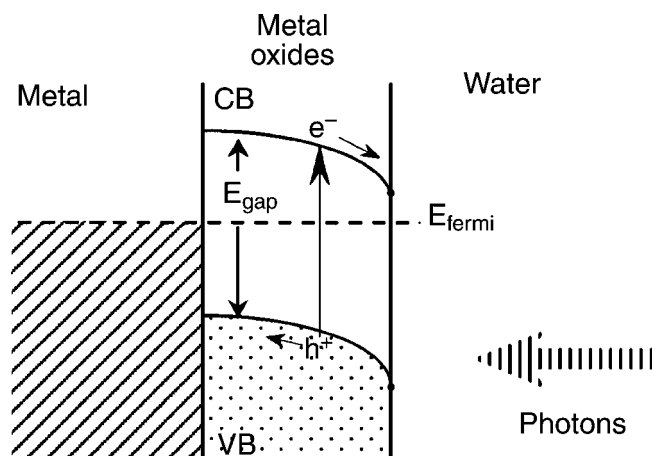


FIGURE 5. For other metals, illumination with UV light creates positively charged holes in the oxide that flow to the metal and gives a positive photo-voltage. The electrons flow to the surface where they accelerate the cathodic reactions.

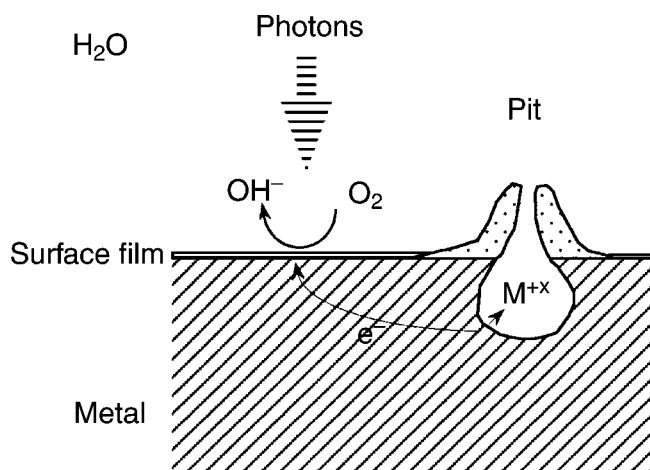


FIGURE 6. Illumination with the UV light accelerates pitting corrosion by accelerating the cathodic reaction on the metal surface.

There are exceptions to the above model. The brass exhibited negative photo-voltages but showed slight photo-inhibition of corrosion in Figure 2. Previous researchers^{6-8,12} reported that UV exposure improved the properties of the passive film on Type 304 SS, and this might be the case for brass as well. Nickel showed a positive photo-voltage, but no photo-corrosion probably because it did not pit in this benign fresh water.

CONCLUSIONS

❖ Zinc, carbon steel, Al 6061, copper, and silver all showed increased corrosion rates under the UV light (photo-corrosion), as compared to duplicate samples immersed upstream in the dark. Therefore, photo-corrosion is a real effect and not simply a laboratory artifact.

❖ The observed effects could be explained either by the UV light modifying the passive film (e.g., brass) or by the measured photo-voltages. A dissolution model was proposed to explain the accelerated uniform corrosion of metals with negative photovoltages, and a pitting model was proposed to explain the accelerated pitting corrosion of metals with positive photo-voltages.

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2003

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