

Highly corrosion-resistant metals for the pulp and paper industry

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Among the metals highly resistant to corrosion in the aggressive environments of pulp mills and bleach plants, zirconium stands out as competitive in terms of costs and performance.

The pulp and paper industry has improved process efficiency and complied with environmental regulations since the 1970s. These steps have created some serious corrosion problems, however, because of the increased corrosiveness of pulping and bleach solutions. The increased corrosiveness of pulping solutions results from higher sulfide and thiosulfate concentrations, and that of bleach solutions results from higher temperatures, higher chloride concentrations, and lower pH values. Common stainless steels, such as Type 316L SS, are no longer resistant to corrosion under these conditions. To cope with corrosion problems, modern pulp mills use materials that are more resistant to corrosion. Here, we present the use of metals more highly resistant to corrosion—zirconium, titanium, and titanium-3% aluminum-2.5% vanadium.

Environmental restrictions require high corrosion resistance

Recently, there has been increasing concern about the presence of extremely small amounts of dioxin in white paper products as well as in river fish. Dioxin is the most potent cancer-causing substance ever tested in animals. The U.S. Environmental Protection Agency (EPA) claimed that dioxins found in both fish and household products come mostly from the same source—paper mills that use chlorine to whiten and strengthen raw pulp. The pulp and paper industry has countered that automobile emissions, forest fires, and the burning of waste also contribute dioxin to the environment.

Nevertheless, the EPA has advised states to require mills to sharply reduce dioxin emissions by mid-1992. The Oregon Department of Environmental Quality has proposed a policy to force mills to reduce emissions to no more than 0.013 parts per quadrillion by June 1992. Moreover, there is a possibility that zero tolerance be required in the future. Currently, many mills can easily

exceed the 0.013 part per quadrillion limit by more than 10,000 times. Papermakers have various plans to curb the discharge of dioxin in their wastewater, such as switching from chlorine bleaching to chlorine dioxide bleaching. Chlorine dioxide produces fewer dioxins as by-products than chlorine.

To meet restrictive environmental regulations, researchers are working to develop papermaking processes free of sulfur and chlorine. In fact, several of these processes are already commercialized, such as various hydrogen peroxide bleaching processes. The advantages of other processes, such as organosolv and HNO_3 pulping processes, are yet to be thoroughly studied and accepted by the industry. The pulping solutions of these newly developed processes are more corrosive than those of conventional processes and require the use of more corrosion-resistant materials in the mills.

Zirconium

Zirconium is one of the few metals that resists attack by strong acids and strong alkalines (1). It is often used to handle reducing acids, such as HCl and H_2SO_4 (<70%) solutions, since most passive metals have difficulty forming protective oxide films in these acids. It is highly resistant to corrosion in oxidizing acids, such as HNO_3 and CrO_3 solutions, unless halides are also present in considerable amounts.

Zirconium's corrosion properties are important to the pulp and paper industry because:

1. Zirconium is ranked as the metal most resistant to corrosion in SO_2 environments (2).
2. Zirconium has excellent corrosion properties in sulfide-containing solutions at temperatures up to 250°C (3-5).
3. Zirconium resists attack by H_2SO_4 at all concentrations up to 70% and at temperatures up to and above boiling (6).

For both zirconium and titanium, the cost is already competitive with that of using other corrosion-resistant

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metals, before allowing for corrosion resistance. This fact is indicated in **Table I**, based on a comparison made recently by the Titanium Development Association (in a technical bulletin titled "Comparison of Titanium and Titanium Alloys to Other Metals"). Furthermore, zirconium and titanium can be clad easily to steel and other metals, using various cladding techniques. The costs can be lowered by using these metals as clad materials.

Laboratory tests of general and localized corrosion

Zirconium, titanium, and titanium-3% aluminum-2.5% vanadium (Ti-3Al-2.5V) were used in this study. Corrosion specimens were prepared from mill-annealed sheets or plates. Welded specimens were made by butt welding using a tungsten inert gas welder. Type 316L stainless steel was included in certain tests for comparison.

Three test methods were employed to evaluate the metals' resistance to general corrosion and localized corrosion:

1. Immersion tests were performed on Type A specimens, 50.8 × 25.4 mm.
2. U-bend tests were performed on Type B specimens, 127 × 19 mm. Stressing was achieved by a two-stage operation to a radius of 15.9 mm, according to specification ASTM G-30. Polytetrafluoroethylene insulators were used to prevent contact between U-bend and bolt. Both longitudinal and transverse specimens were used. The weld bead of U-bends was parallel to the specimen length.
3. Constant strain-rate tests were performed on Type C tensile specimens, 11.1 mm in diameter × 102 mm long with gauge length 6.4 mm in diameter × 25.4 mm long. The strain rate was $2.5 \times 10^{-6} \text{ s}^{-1}$.

Most of the test solutions were prepared from reagent-grade chemicals. They were kraft, H_2O_2 , HCOOH , and $\text{NaCl}+\text{Cl}_2$ solutions. Also, plant white liquor was provided by a pulp mill for corrosion testing.

Because of the high corrosiveness of kraft solutions, eight 2-L zirconium vessels were made for hot alkaline solutions (**Fig. 1**). The vessels were made from Zr sheet by deep drawing. Zirconium autoclaves were used for corrosion tests at elevated temperatures. However, in constant strain-rate tests in kraft solutions, we used an Alloy C autoclave. Glass containers were used in other tests.

Corrosion tests of zirconium in different kraft solutions

Kraft pulp digesters are constructed mostly from carbon steel, although stainless steels are used to some extent. Deterioration of digesters is one of the major problems in the pulp and paper industry. Deterioration results from general corrosion, galvanic corrosion, and stress corrosion cracking. Since zirconium can be easily clad to carbon steel, the use of zirconium-clad digesters could be a cost-effective alternative for the pulp and paper industry. Consequently, the corrosion properties of zirconium in kraft solutions have been studied.

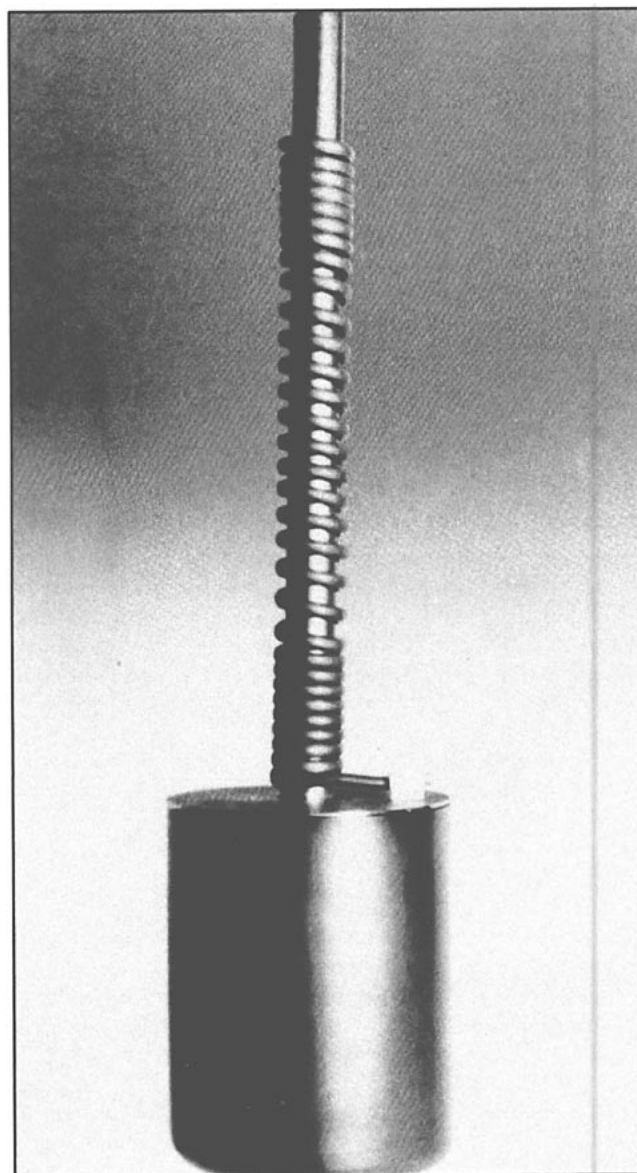
We tested welded and nonwelded coupons of zirconium in a plant white liquor (pH = 14) at 120°, 175°, and 225°C for four days using zirconium autoclaves. All coupons

I. Comparison of fabricated products

Metal	Vessels	Heat exchangers
Type 316L SS	1	1
Ti Grade 2	2.9	2.2
Ti Grade 7	3.7	3.0
Ti Grade 12	3.0	2.4
Ni-Cr-Fe (N06600)	3.1	2.5
Alloy 20	2.1	1.8
Zr Grade 702	3.8	3.0
Ni-Mo (N10665)	4.5	3.6
Ni-Cr-Mo (N10276)	4.3	3.5

The comparison ratios to Type 316L SS were based on structural efficiency and fabrication costs. These ratios are the costs of producing vessels or heat exchangers with the different materials divided by the cost of producing the same product with 316L SS. Allowances for corrosion resistance were not included.

1. A 2-L zirconium vessel equipped with a zirconium condenser wrapped by a copper cooling coil



II. Results of constant strain rate tests for zirconium

Medium	Max. stress, MPa		Max. strain, %	
	Longi- tudinal	Trans- verse	Longi- tudinal	Trans- verse
1. 100 g/L NaOH + 33 g/L Na ₂ S	345	340	30.9	33.0
2. 100 g/L NaOH + 33 g/L Na ₂ S + 18 g/L Na ₂ S ₂ O ₃	340	349	28.7	32.8
3. 100 g/L NaOH + 33 g/L Na ₂ S + 18 g/L Na ₂ S ₂ O ₃ + 50 g/L NaCl	354	336	29.7	27.3
4. Distilled H ₂ O	...	331	...	27.6

Tests at 90°C and $2.5 \times 10^{-6} \text{ s}^{-1}$.

showed corrosion rates of less than 0.025 mm/year. These results indicate that zirconium is suitable as a structural material for liquor heaters. In the same liquor, graphite and glass both corroded rapidly at 100°C.

Resistance to stress corrosion cracking is an important requirement for the structural materials of kraft pulp digesters. U-bend and constant strain-rate tests were used to assess the stress corrosion cracking resistance of zirconium in three solutions at 90°C:

1. 100 g/L NaOH + 33 g/L Na₂S
2. 100 g/L NaOH + 33 g/L Na₂S + 18 g/L Na₂S₂O₃
3. 100 g/L NaOH + 33 g/L Na₂S + 18 g/L Na₂S₂O₃ + 50 g/L NaCl.

Four U-bends of zirconium were tested in each kraft solution for 60 days. Conditions of U-bends were longitudinal cut nonwelded, transverse cut nonwelded, longitudinal cut with weld, and transverse cut with weld. All U-bends showed no cracking. Also, no corrosive attack was observed. Overstressing the tested U-bends indicated that they remained ductile.

Results of constant strain-rate tests are given in **Table II**. As can be seen, the addition of NaOH, Na₂S, Na₂S₂O₃ and NaCl to H₂O has little effect on the tensile properties of zirconium. Tested tensile specimens did not show any secondary crack either. Interestingly, the Alloy C autoclave used in these tests showed increasing deterioration with each test.

In addition, zirconium is highly corrosion resistant in alkaline solutions that are stronger than kraft solutions. In fact, results of plant tests indicated that zirconium outperformed nickel, monel, inconel, and titanium in various alkaline solutions and a caustic fusion (?). This quality makes zirconium distinctly different from some other highly corrosion-resistant materials, such as tantalum, glass, graphite, and PTFE, which are attacked by strong alkali.

Corrosion resistance of zirconium to hydrogen peroxide

Hydrogen peroxide is reputed to be a safe oxidant since its decomposition products are water and oxygen. It is

being used more and more in various bleaching methods in the pulp and paper industry. In selecting materials for H₂O₂ process equipment, one should consider the corrosiveness and stability of H₂O₂. Corrosion data of metals in H₂O₂ are limited and sometimes misleading. The growing importance of H₂O₂, together with new H₂O₂ production processes, warrants the need for a better understanding of the corrosion properties of equipment materials. Hydrogen peroxide is not a stable compound since it decomposes upon heating or in the presence of numerous substances, particularly salts of such metals as iron, copper, manganese, nickel, or chromium. When the stability of H₂O₂ is a concern, iron- or nickel-base alloys may not be suitable equipment materials, even when they show adequate corrosion resistance in H₂O₂-containing environments. After all, H₂O₂ is a much more valuable commodity than H₂O + O₂.

One of the earliest applications for zirconium was in the production of H₂O₂ using H₂SO₄, by FMC Corp. at Vancouver, Wash. (8). Zirconium heat exchangers were chosen to replace impervious graphite exchangers that had lasted about 12-18 months. Zirconium exchangers provided a service life of 9-10 years before maintenance was required. The zirconium exchanger tube walls would be thinned at the liquid-gas interface due to bubble collapse, but no other corrosion occurred. Consequently, zirconium is being evaluated for its corrosion resistance in H₂O₂ environments.

We tested coupons of zirconium, titanium, and Type 316L SS in H₂O₂ solutions at 70°C for 48 h. Test results are given in **Table III** and indicate a number of findings. First, as-mixed 5% and 10% H₂O₂ solutions are mildly acidic and are not highly corrosive. The adjustment of pH to more acidic or more basic can markedly increase the corrosivity of H₂O₂ solutions. In the bleaching operation, alkaline H₂O₂ solutions are commonly employed.

Second, corrosion rates of Type 316L SS in the as-mixed solutions are low. However, there was a sharp drop in pH during corrosion testing. Spent H₂O₂ solutions became acidic water.

Third, corrosion rates of titanium are much higher than those of zirconium in H₂O₂ solutions. This difference may

III. Results of immersion tests in H_2O_2 solutions at 70°C for 48 h

Metal	H_2O_2 , %	pH ^a		Corrosion rate, mm/y	
		Before	After	Nonwelded	Welded
Zirconium	5	4.54	4.65	< 0.01	< 0.01
Titanium	5	4.54	4.43	0.19	0.28
Type 316L SS	5	4.54	1.76	< 0.01	...
Zirconium	5	1	1.43	< 0.01 ^b	0.05 ^b
Titanium	5	1	1.33	0.61	0.81
Type 316L SS	5	1	1.09	3.12	...
Zirconium	5	9.5	11.45	< 0.01	< 0.01
Titanium	5	9.0	11.66	0.36	0.38
Type 316L SS	5	9.2	12.05	< 0.01	...
Zirconium	10	4.25	4.18	< 0.01	< 0.01
Titanium	10	4.25	4.09	0.58	0.78
Type 316L SS	10	4.25	2.02	< 0.01	...
Zirconium	10	1	1.28	< 0.01	0.09 ^b
Titanium	10	1	1.30	1.17	1.68
Type 316L SS	10	1	1.10	0.91	...
Zirconium	10	8.9	12.03	< 0.01	< 0.01
Titanium	10	9.0	12.01	0.43	0.46
Type 316L SS	10	8.9	12.02	< 0.01	...

^aThe solution pH was measured at room temperature before and after corrosion testing. The pH values of the as-mixed 5% and 10% H_2O_2 were 4.54 and 4.25, respectively. HCl or NaOH was used to adjust pH to 1 or 9.

^bZirconium coupons showed some minor localized corrosion, particularly in the heat affected zone.

be due to the soluble peroxo complexes of titanium as compared to the sparingly soluble hydrated peroxides of zirconium formed in H_2O_2 solutions.

Fourth, zirconium showed some susceptibility to localized corrosion in H_2O_2 solutions at pH 1. The least corrosion-resistant area was the heat-affected zone, and the most resistant area was the weld metal, which showed no sign of corrosion. This susceptibility can be attributed to the high oxidizing power of H_2O_2 and the presence of chloride ions, but it cannot be ascribed to the low pH. Zirconium has excellent corrosion resistance in H_2O_2 + H_2SO_4 solutions, as it showed in the production of H_2O_2 . However, zirconium has a tendency to show localized corrosion in oxidizing chloride solutions. Corrosion control methods given elsewhere (9) can be considered for zirconium in H_2O_2 +HCl solutions. They include surface conditioning, heat treatment, and electrochemical protection.

Corrosion resistance of zirconium in formic acid pulping processes

Organosolv pulping with a variety of solvents such as ethanol, formic acid, acetic acid, and other delignifying solvents containing no sulfur is still being suggested as a suitable processing alternative (10-12). Solutions of H_2SO_4 , HNO_3 , and NaOH have also been suggested as chemicals on which to base processing alternatives.

There are many other new processes that offer advantages like energy savings, valuable by-products, and environmental safety. Zirconium's excellent corrosion resistance in mineral acids, organic acids, and caustics indicates that it would be a suitable structural material for most of these processes. To illustrate this contention, we have reviewed the use of zirconium in the formic acid

pulping process, since a zirconium vessel is being used for the developmental work at the Finnish Pulp and Paper Research Institute (FPPRI).

This pulping process uses a mixture of HCOOH and H_2O_2 (12). Under the cooking conditions, these form peroxyformic acid, which can selectively delignify wood. The lignin is oxidized, broken down, and dissolved in the cooking liquor, while the wood polysaccharides are relatively unaffected. To reduce the consumption of H_2O_2 , this process has three cooking stages. The first is HCOOH cooking in the presence of small amounts of H_2O_2 at 80°C. The second stage involves refluxing in HCOOH without H_2O_2 at 100°C. The third stage is another peroxyformic acid cooking at 80°C. The pulp can be bleached by alkaline H_2O_2 .

Formic acid is an excellent solvent but is highly corrosive to many metals. Titanium has shown some inconsistency in HCOOH. Factors such as aeration and lack of water strongly affect titanium's resistance to HCOOH. Stainless alloys also have some serious limitations. For example, Type 316L SS can be rapidly attacked by intermediate strengths of hot HCOOH. Nickel-base alloys may corrode at high rates in the presence of halides and under heat transfer conditions (13).

In contrast, zirconium's corrosion resistance in HCOOH is outstanding (14). Below the boiling point at 98% concentration, and up to 150°C and 90% concentration, zirconium's corrosion rate is less than 0.025 mm/year. The corrosion resistance of zirconium in HCOOH is not affected by aeration, heat transfer, and impurities like Cl^- , I^- , SO_4^{2-} , Fe^{3+} , or Cu^{2+} . Consequently, zirconium-clad reactors and distillation columns are being used in the manufacture of HCOOH from CO and H_2O (15). Other pieces of zirconium

equipment include heat exchangers, piping, pumps, and valves.

The suitability of zirconium for HCOOH pulping has been demonstrated by FPPRI. However, actual corrosion data are not available. Therefore, welded and nonwelded coupons of zirconium were tested in HCOOH (50% and 80%) with H₂O₂ (2% and 4%) solutions at 80°C for 24 h. Corrosion of zirconium under these conditions was less than 0.01 mm/y, confirming the suitability of this material for HCOOH+H₂O₂ cooking conditions.

Corrosion tests of titanium and Ti-3Al-2.5V

Titanium is well known for its excellent corrosion resistance in seawater and many chlorine salts, particularly under oxidizing conditions. This resistance makes titanium attractive for application in many areas of the bleach process using chlorine compounds. The pulp and paper industry has recognized titanium's usefulness for over 30 years. The earliest application of titanium was a titanium-lined ClO₂ mixer installed in 1955 at the St. Regis Paper Co. in North Carolina (16). This unit has performed well. Since this successful use, titanium has found many uses in bleach plants: ClO₂ systems (generator, evaporator, crystallizer, and regenerator reboiler), diffusion pulp thickening and washing systems, drum washers, hypochlorite storage, and wet Cl₂ systems (17-19).

Recently, interest has been increasing in the nonaerospace applications of Ti-3Al-2.5V. Ti-3Al-2.5V has certain unique, attractive properties including lightweight, high strength, torsion resistance, biocompatibility, cold formability, fabricability, and corrosion resistance. The structural efficiency (maximum allowable design stresses adjusted for density) of Ti-3Al-2.5V is much better than that of titanium, Alloy C-276, or Alloy 625 (20). Corrosion properties of Ti-3Al-2.5V parallel those of titanium (21). Ti-3Al-2.5V may also be suitable for bleaching applications using highly oxidizing chlorine compounds.

Nonwelded and welded U-bends of titanium and Ti-3Al-2.5V were tested in Cl₂-saturated NaCl (2.5 g/L Cl₂) solutions at 50°C for 120 days. The solution pH was adjusted to 1.5 or 4. Test solutions were changed weekly. Dissolved Cl₂ was about 200 ppm. All U-bends showed negligible corrosion rates. There was no evidence of crevice corrosion under the bolt and nut areas. No cracking was found on the nonwelded U-bends of titanium and Ti-3Al-2.5V. However, fine cracks were found within the heat-affected zone of welded U-bends of titanium and Ti-3Al-2.5V. The stress corrosion cracking susceptibility of Ti-3Al-2.5V appeared to be close to that of titanium in Cl₂-saturated NaCl solutions. Stress relief of the weld metals of titanium and Ti-3Al-2.5V can be a safeguard for use in highly oxidizing solutions of chlorine compounds.

Conclusions

Zirconium, titanium, and Ti-3Al-2.5V have been evaluated for their suitability in various pulping and bleaching processes. The following conclusions can be drawn:

1. Zirconium is highly resistant to general corrosion and stress corrosion cracking in kraft liquors.
2. Zirconium is more resistant than titanium and stainless steels in H₂O₂ solutions. However, the presence of

chlorides should be avoided in acidic H₂O₂ solutions.

3. Zirconium may be suitable for use in certain new pulping and bleaching processes, particularly the ones using HCOOH and H₂O₂.
4. The corrosion resistance of Ti-3Al-2.5V is similar to that of titanium in Cl₂ saturated NaCl solutions. Stress relief is recommended for the weld metal. □

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