# Zirconium in Nitric Acid/Ammonium Nitrate Plants

*By Rob Henson*

Nitric acid and ammonium nitrate producers are choosing zirconium equipment because its life cycle cost is superior to stainless steel even though its per-pound cost is higher. Figure I shows a cooler condenser built in 1997 that we expect to last for more than 25 years (see other cooler condenser photos on page 30). Weatherly installed the world's first zirconium cooler condenser in 1984 when it upgraded Mississippi Chemical's existing acid plant to a high mono-pressure type to increase capacity and efficiency.[1] However, mono-pressure plants are not the only ones to use zirconium; acid distillation units also use it.[2] More than 40 acid plants now have zirconium in them.

Engineers no longer consider zirconium to be an exotic material but rather a material that is suitable for constructing the largest chemical process equipment. When comparing the cost of zirconium equipment with stainless steel, factors to consider include:

1. Zirconium has a 20 percent lower density than common stainless steel.
2. Zirconium has a 35 percent higher thermal conductivity than common stainless steel.
3. Zirconium equipment does not require a corrosion allowance.

These factors will often reduce the zirconium/stainless steel price ratio to the 2.5 to 4.0 range. When the overall life-cycle costs are fully evaluated, zirconium equipment's lower maintenance cost and longer life will show a substantial savings. Also, stable zirconium prices have contributed to its market growth. Zirconium is easy for fabricators to use, but its chief characteristic is its exceptional resistance to corrosion.

## *Corrosion*

A protective surface oxide film, which is almost as hard as sapphire, shields zirconium from corrosive and abrasive environments. Equipment manufacturers do not have to purposely oxidize freshly exposed metal because machined, pickled, or sawn surfaces readily oxidize at ambient temperature. However, we do recommend that manufacturers oxidize high-stress items, such as pump shafts and nuts and bolts, under controlled conditions at higher than ambient temperatures. A shiny, dark blue to black surface film, approximately 20 micrometers thick, is the hallmark of a high-quality finish. Zirconium's higher heat transfer coefficient, lower thermal expansion coefficient, and lower-fouling characteristic markedly reduce the size and complexity of zirconium equipment. Table 1 lists zirconium's physical properties.[3]

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**Figure I — Cooler Condenser Built in 1997**

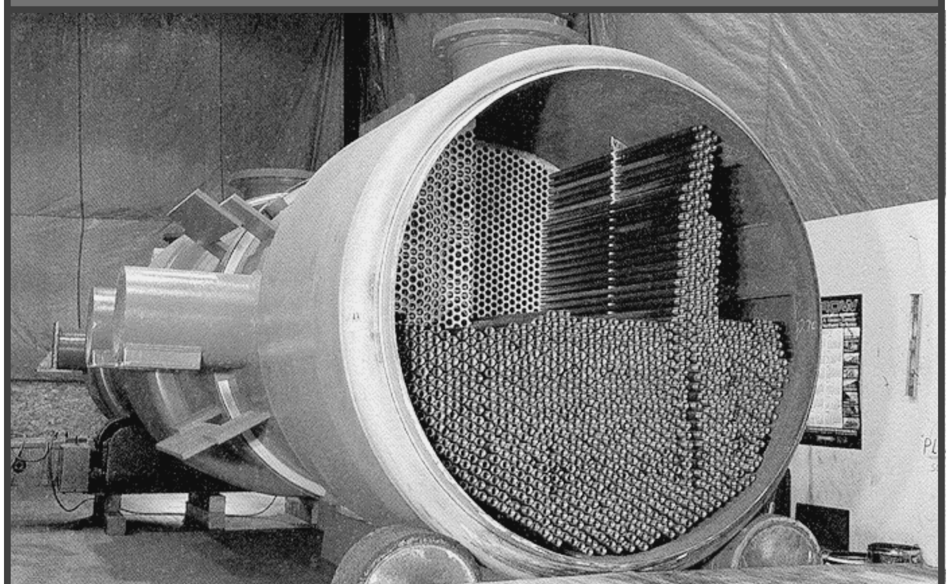

**Table 1 — Physical Properties**

| | Zr 702 | Zr 705 |
|---|---|---|
| Melting Point | 1,852°C (3,365°F) | 1,840°C (3,344°F) |
| Boiling Point | 4,377°C (7,910°F) | 4,380°C (7,916°F) |
| Specific Heat, BTU/lb/°F (32-212°F) | 0.068 | 0.067 |
| Vapor Pressure (mm Hg) | | |
| 2,000°C (3,632°F) | 0.01 | – |
| 3,600°C (6,512°F) | 900 | – |
| Thermal Conductivity (300-800K) Watts/m-k (BTU-ft/hr-ft$^2$°F) | 22.0 (13.0) | 17.1 (10.0) |
| Coefficient of Thermal Expansion, mm/mm/°C X $10^{-6}$ (in/in/°F x $10^6$) | | |
| 37.8°C (100°F) | 1.78 (3.2) | – |
| 148.9°C (300°F) | 1.94 (3.5) | – |
| 260°C (500°F) | 2.16 (3.9) | – |
| 371.1°C (700°F) | 2.27 (4.1) | – |
| Latent Heat of Fusion (Cal/gm) | 60.4 | – |
| Latent Heat of Vaporization (Cal/gm) | 1,550.0 | – |
| Modulus of Elasticity, Gpa(psi X $10^6$) | | |
| Room Temperature | 99.2 (14.4) | – |
| 37.8°C (100°F) | 98.6 (14.4) | – |
| 93.3°C (200°F) | 93.1 (13.5) | – |
| 148.9°C (300°F) | 86.9 (12.6) | – |
| 204.4°C (400°F) | 80.7 (11.7) | – |
| 260°C (500°F) | 75.2 (10.9) | – |
| 315.6°C (600°F) | 69.6 (10.1) | – |
| 371.1°C (700°F) | 64.12 (9.3) | – |
| Shear Modulus of Elasticity, Gpa (psi X $10^6$) | | |
| Room Temperature | 36.2 (5.25) | 34.5 (5.0) |
| Poisson's Ratio | | |
| Room Temperature | .035 | .033 |
| Density, g/cm$^3$ (lbs/in$^3$) at 20°C (68°F) | 6.51 (0.235) | 6.64 (0.240) |

ZIRCONIUM ... (Cont. from page 28)

Although the nitric acid industry has traditionally used stainless steel, Figure II indicates that zirconium is far more resistant to corrosion than stainless steel at higher temperatures in the condensing zone. Figure III shows zirconium's excellent corrosion resistance in nitric acid over a very wide range of temperatures and concentrations. It performs the same as more noble metals, such as niobium and tantalum. Only platinum outperforms zirconium in nitric acid service.[4]

Zirconium's corrosion resistance is not sensitive to changes in acid concentration, temperature, or its metallurgical condition and the presence of ferric chloride, sea water, sodium chloride, chlorine, iron, nickel, or chrome do not lower its corrosion resistance. Zirconium needs special attention to avoid corrosion in the following environments:

1. Strong acid. Stress corrosion cracking can occur in 70 percent nitric acid or higher. (Stress relieving welds and/or exchanger design can eliminate this problem.)
2. Fluoride contamination. Fluoride ions can corrode zirconium at rates proportional to the fluoride concentration. (Operators should avoid contaminated water with non-complexed fluoride ions.)
3. Chloride contamination.Vapor phase mixtures of nitric acid and chlorides can cause pitting. (Chlorine gas may be the corrosive agent. A good surface finish can alleviate the problem.)

However, in normal nitric acid service, zirconium poses few concerns. As with any equipment that must handle hazardous chemicals, careful design and planning provide the best assurance of success.

### *Corrosion Products*

Zirconium's resistance to corrosion is also useful for improving nitric acid purity. Even trace amounts of dissolved corrosion products are sometimes unacceptable. Downstream processes for manufacturing plastics, pharmaceuticals, and computer chips can require ultra-pure nitric acid.

### *Fabrication*

Reactive metals require an inert gas shield during welding. Most fabricators choose gas tungsten arc welding (GTAW), but recent advances in technology have allowed them to use plasma and metal inert gas (MIG) equipment as well. To prevent tungsten contamination, we recommend welders start with a direct current, high frequency arc, and a consumable zirconium electrode. Shielding gas must continue to flow after welding stops until the metal cools to below 300°C.[5]

Zirconium welds do not need heat-treating except those in concentrated sulfuric acid service or in stress corrosion environments. Sulfuric acid can cause intergranular corrosion. Designers of zirconium equipment for 70 percent nitric acid, or stronger, should minimize residual stresses and require all welds to be heat-treated.

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**Figure II Corrosion Comparison at Higher Temperatures**

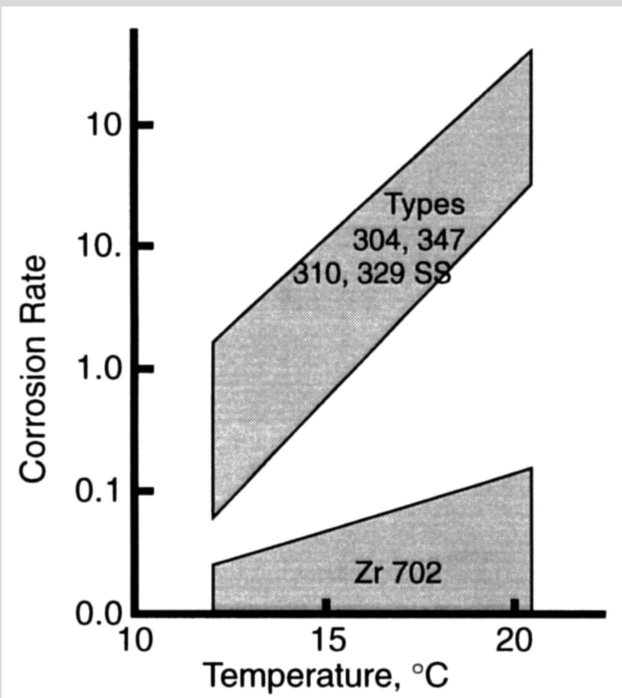
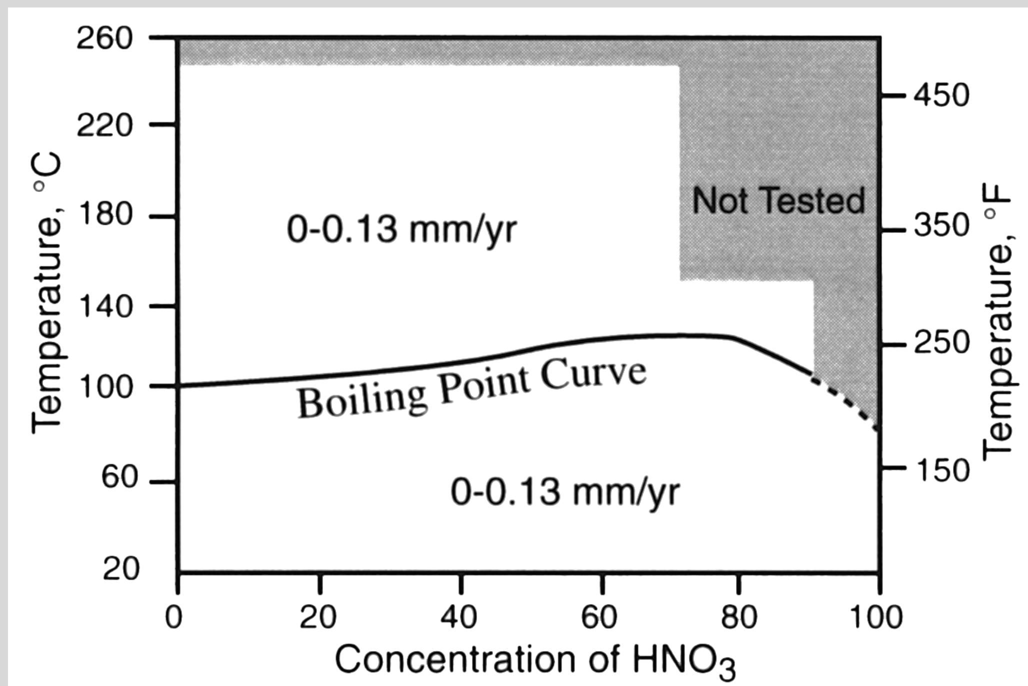



**Figure III Zirconium's Corrosion Resistance in Nitric Acid Over Wide Range of Temperatures and Concentrations**



ZIRCONIUM ... (Cont. from page 29)

Zirconium welds may be heat-treated at 550°C to 600°C for one hour per inch of thickness. Heat treatment for optimum corrosion resistance to sulfuric acid should be performed at 630°C to 788°C.[6] Heat-treating may be done in the atmosphere because the temperature is not high enough for the base metal to absorb oxygen.

Plants must have robust piping systems to withstand corrosion and prevent fugitive emissions. Zirconium's corrosion resistance, strength, and weldability make it suitable for piping and piping components. Welded zirconium joints are corrosion-resistant and leak-free. For those piping connections that cannot be welded, flanged connections are available. Gaskets for flanged joints should not contain graphite or recycled fluorocarbon polymers. Graphite has caused galvanic corrosion in hydrochloric acid service and recycled fluorocarbon polymers may release fluorides that can attack zirconium. Gaskets made of virgin fluorocarbon have performed satisfactorily.

## *Safety*

Ammonium nitrate plant materials of construction have recently come under scrutiny for safety reasons. Zirconium would be ideally suited for nitric acid preheating, sparging equipment, and neutralizer vessel linings. ■

[1] *Outlook*, Vol. 6, No. 4, Teledyne Wah Chang, 1985.

[2] *Outlook*, Vol. 4, No. 3, Teledyne Wah Chang, 1983.

[3] Yau, T.L., "Corrosion of Zirconium," *Corrosion Engineering Handbook*, p. 199.

[4] Yau, T.L., "Zirconium for Nitric Acid Solutions," *Industrial Applications for Titanium and Zirconium: Fourth Volume*, 1986, pp. 56-68.

[5] Etienne, S., "Welding and Heat Treating in Zirconium Alloys: Practical Aspects and Recent Examples of Realization," *Zirconium/Organics Conference*, 1997. pp. 125-138.

[6] *Outlook*, Vol. 13, No. 1, Teledyne Wah Chang, 1992.

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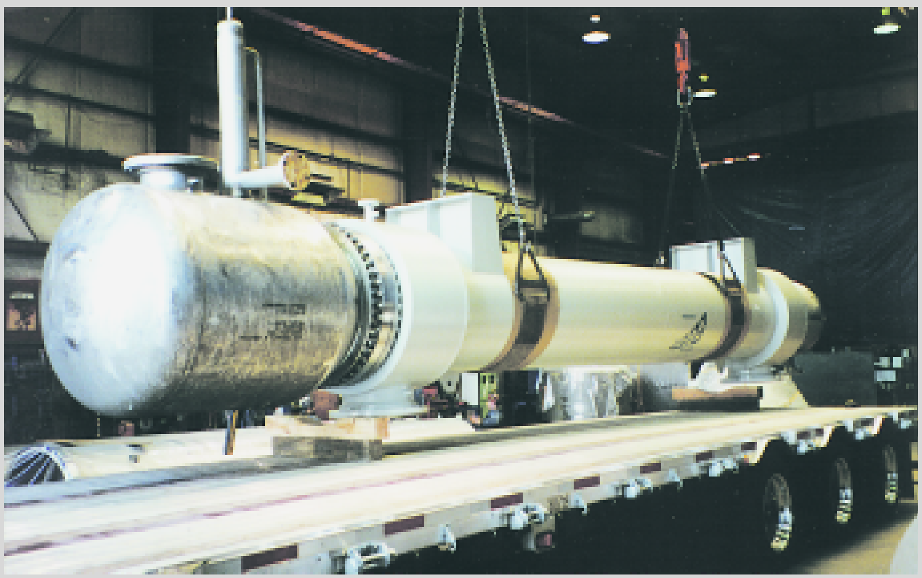
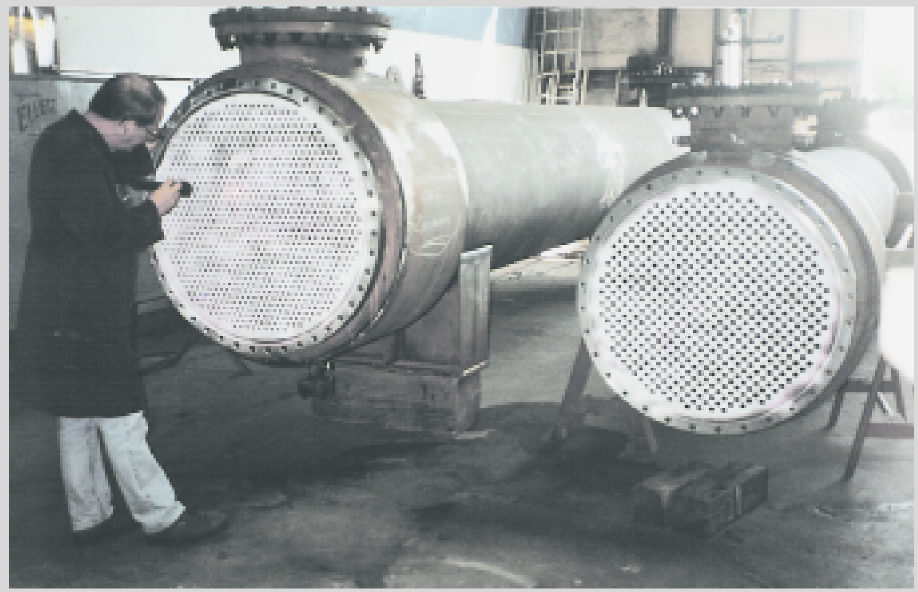
*Cooler condensers with Zirconium 702 tubes and zirconium clad tubesheets being inspected and readied for shipment at Ellett Industries' factory in Port Coquitlam, British Columbia. Ellett has supplied similar cooler condensers to:*





**Esso Chemicals** ........ *Redwater, Alberta, Canada*
**Air Products** ........ *Pasadena, Texas*
**Air Products** ........ *Pace, Florida*
**Monsanto** ........ *Pensacola, Florida*
**Agrium** ........ *Beatrice, Nebraska*
**LaRoche Industries** ........ *Crystal City, Missouri*
**Farmland Industries** ........ *Coffeyville, Kansas*
**Farmland Industries** ........ *Fort Dodge, Iowa*
**ICI (2)** ........ *Gladstone, Queensland, Australia*
**Youngnam Chemicals** ........ *Pusan, South Korea*
**Terra Nitrogen** ........ *Port Neal, Iowa*
**Simplot Canada** ........ *Brandon, Manitoba, Canada*