Zirconium in Nitric Acid Applications

INTRODUCTION

Nitric acid is one of the most widely used acids in the Chemical Processing Industry. It is a key raw material in the production of ammonium nitrate for fertilizer, and is also utilized in a variety of manufacturing processes,including the production of industrial explosives, dyes ,plastics, synthetic fibers, metal pickling and the recovery of uranium. As the demands on nitric acid process equipment have increased, material selection for that equipment has become crucial. Suitable structural materials need to be cost effective, reliable, durable, efficient, and non-contaminating to the product and the environment. For over 20 years, zirconium has proven to be the best solution for many nitric acid applications (**Table 1**).

Most nitric acid is produced by the oxidation of ammonia with air over platinum catalysts. The resulting nitric acid is further oxidized into nitrogen oxide and then absorbed into water to form HNO_3. This process produces acid of up to 70% concentration, with higher concentration acid produced by distilling the dilute acid with a dehydrating agent. Stainless steel has long been used in nitric acid applications; however, it has developed certain serious problems over the years and is subject to several limitations. The superior corrosion resistance of zirconium can overcome some of these limitations,making it an ideal replacement material in many specific nitric acid environments.

TABLE 1: MAJOR NITRIC ACID PROCESSES SUITABLE FOR ZIRCONIUM USE

Synthesis of Nitric Acid
Synthesis of Adipic Acid (without an oxidizing catalyst)
Nitration of Organics
Reprocessing of Spent Nuclear Fuels
Ammonium Nitrate and other Nitrate Salts

CORROSION DATA

The excellent corrosion resistance of zirconium in nitric acid has been recognized for more than 30 years. As shown in the isocorrosion diagram (**Fig.1**), the corrosion rate of zirconium is conservatively stated as less than 5 mpy (mils per year) at concentrations up to 98% HNO_3 and temperatures below the boiling point, as well as 70% HNO_3 and up to 250C.

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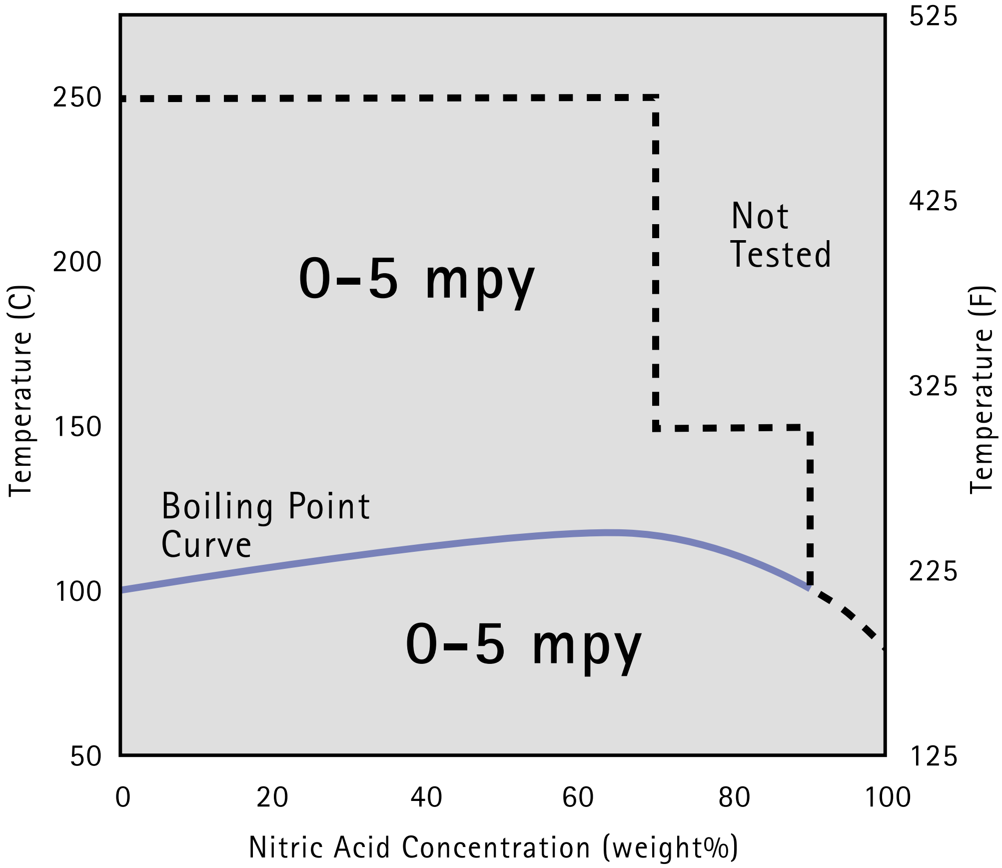
FIGURE 1: THE ISOCORROSION CURVE FOR ZIRCONIUM IN NITRIC ACID



Another strength of zirconium is its ability to handle a wide variety of impurities commonly found in nitric acid environments, with little or no effect on corrosion rate. The presence of $FeCl_3$, Cr^{+6}, seawater, NaCl, chlorine (Cl_2), iron or stainless steel does not degrade zirconium 's resistance to HNO_3 (**Table 2**). While zirconium is normally susceptible to pitting in acidic oxidizing chloride solutions,the NO_3- ion effectively inhibits this phenomenon.

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TABLE 2: CORROSION RATE OF ZIRCONIUM IN HNO_3 WITH IMPURITES (TEMPERATURES HELD AT BOILING POINT FOR 8 DAYS)

		Corrosion Rate (m/year)			
		Liquid Phase		Vapor Phase	
Nitric Acid, %	**Impurity**	**Nonwelded**	**Welded**	**Nonwelded**	**Welded**
30/50/70	0.1 or 1% $FeCl_3$	<2.5	<2.5	<2.5	<2.5
30/50/70	0.1 or 1% seawater	<2.5	<2.5	<2.5	<2.5
30/50/70	0.1%NaCl	<2.5	<2.5	<2.5	<2.5
30	1% NaCl	<2.5	<2.5	<2.5	<2.5
50	1% NaCl	<2.5	<2.5	12.7	35.6
70	1% NaCl	<2.5	<2.5	<2.5	<2.5
0	Saturated Cl_2	<2.5	102	<2.5	91.4
30	Saturated Cl_2	<2.5	<2.5	<2.5	<2.5
50	Saturated Cl_2	<2.5	<2.5	<2.5	<2.5
70	Saturated Cl_2	<2.5	<2.5	<2.5	<2.5
30/50/70	1% Fe	<2.5	<2.5	<2.5	<2.5
30/50/70	1.45% 304 S.S.	<2.5	<2.5	<2.5	<2.5

Although stress corrosion cracking has been a concern for using zirconium in nitric acid,results of U-bend tests indicate that zirconium has excellent resistance to stress corrosion cracking in relatively high HNO_3 concentrations and elevated temperatures (**Table 3**). Tests have also shown that impurities have little effect on the susceptibility of zirconium to stress corrosion cracking at nitric acid concentrations up to 70% and room temperature. Proper equipment design and stress relieving at elevated temperatures can help to mitigate this problem at higher concentrations.

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TABLE 3: RESULTS OF U-BEND TESTS FOR ZR IN NITRIC ACID (TOTAL TEST EXPOSURE OF 7 DAYS)

Condition	**Nitric Acid (%)**	**Temperature (C)**	**Time to Failure (Days)**
As-welded	65	149	Did not fail
As-welded	65	204	Did not fail
Longitudinal	65	204	Did not fail
Transverse	65	204	Did not fail
As-welded	70	149	4
As-welded	70	204	1
Longitudinal	70	204	Did not fail
Transverse	70	204	Did not fail

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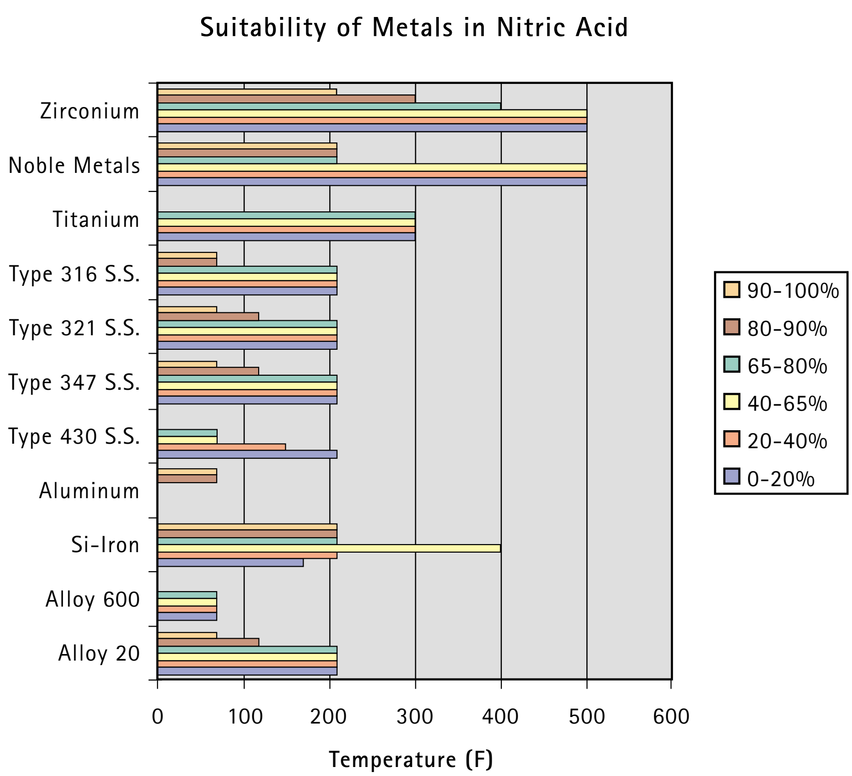
ADVANTAGES OF ZR OVER OTHER MATERIALS

Because of its passivating power, nitric acid is not considered to be a difficult acid for passive metals to handle. Nevertheless, it does become highly corrosive to most metals at elevated temperatures, very high or very low concentrations, or when impurities are present. Zirconium is considerably more suitable than most passive metals for handling HNO_3 under these conditions,and its performance is even better than the noble metals in some cases (**Fig. 2**).

FIGURE 2



Stainless steel has long been used in nitric acid plants, and it does exhibit good corrosion resistance over a wide range of concentrations and temperatures in nitric acid. There are still considerable problems with stainless steel, particularly in pressurized HNO_3 at elevated temperatures. As shown in **Figure 3** and **Table 4**, stainless steel suffers significant corrosion as nitric acid concentration increase. The presence of chromium in certain products resulting from the corrosion of stainless steel has also become a serious concern, as this poses an environmental hazard. Data for specifically selected competitor alloys is listed in **Table 5**.

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FIGURE 3: CORROSION OF VARIOUS ALLOYS IN NITRIC ACID AT 190C

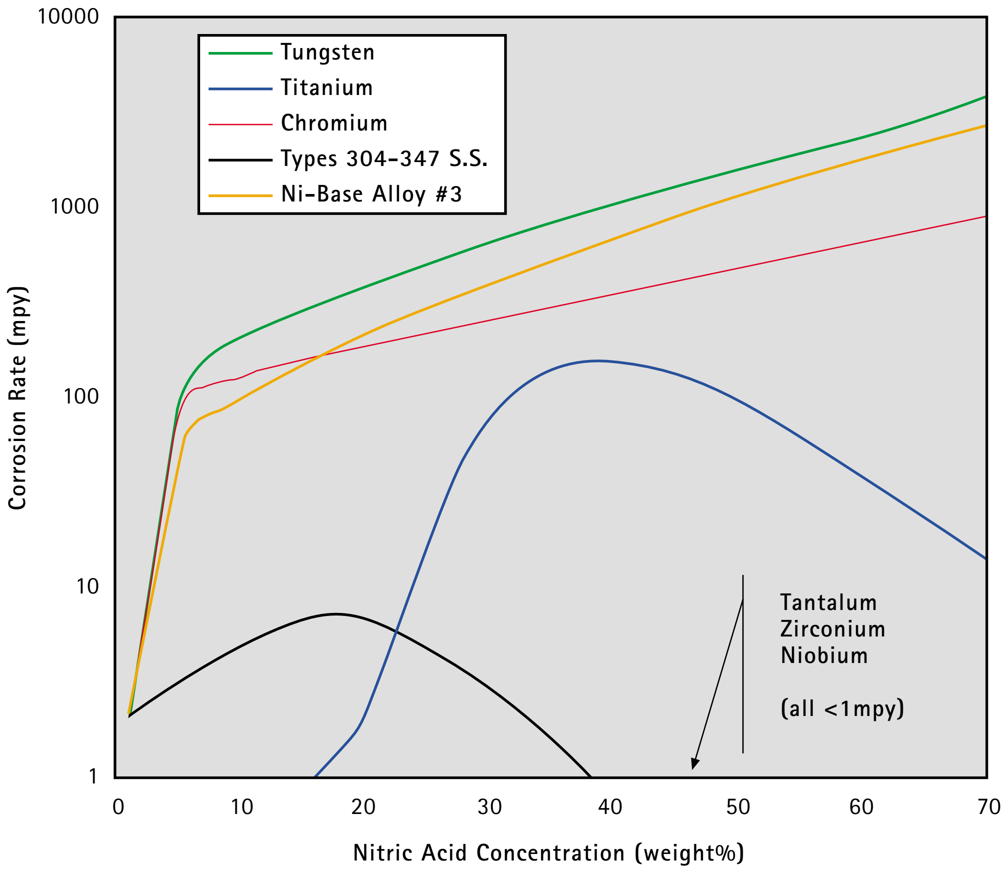

TABLE 4: CORROSION RATE OF STAINLESS STEELS IN 65% NITRIC ACID AT 204°C

Alloy	Test Duration (hours)	Corrosion Rate (mpy)
Zr 702	48	0.3
304L S.S.	3	>15,000
310L S.S.	20	>12,000
316L S.S.	20	>15,000

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TABLE 5: CORROSION OF ZIRCADYNE 702 VS. COMPETITOR ALLOYS IN 65% NITRIC ACID AT ELEVATED TEMPERATURES

	Corrosion Rate (mpy)		
Alloy	121C (250F)	149C (300F)	204C (400F)
Carpenter 7-Mo	9.5	480	2482
Carpenter 7-Mo Plus	7.9	---	---
Carpenter 7-Mo Plus (welded)	9.1	---	---
Sandvik 2RE10	4.9	86	1064
Uddeholm 44 LN	5.4	315	---
Uddeholm 44 LN (welded)	10.3	336	---
Uddeholm 25 L	5.3	166	---
Uddeholm 25 L (welded)	8.1	116	---
VDM 2521 LC	35	410	7600
VDM 2522 LCN	36	580	12500
Zircadyne 702	0.0	0.0	0.0
Zircadyne 702 (welded)	0.0	0.0	0.0

Titanium can sometimes be used to solve the problems of stainless steel in nitric acid, however its corrosion behavior is complicated. In contrast to stainless steel, titanium's corrosion resistance actually improves as the level of some impurities increases in nitric acid. Unlike zirconium, however, titanium cannot naturally form a stable, protective oxide film on its surface in pure nitric acid, which restricts its use in hot, pure solutions or vapor condensates of nitric acid. Titanium is also very sensitive to the presence of titanium ions resulting from corrosion (**Table 6**).

TABLE 6: EFFECT OF TITANIUM ION ON CORROSION IN BOILING NITRIC ACID (24 HOUR TEST)

Ti+4 Ion Concentration (ppm)	**Corrosion Rate (mpy)**	
	40% HNO_3	68% HNO_3
0	30	32
20	8.7	2.4
40	2.0	0.4
80	0.8	0.4

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Based on these limitations,zirconium becomes the clear choice as the material of construction for critical nitric acid processing equipment.The superiority of its corrosion resistance under different operating conditions, and the elimination of the resulting corrosion by-products give zirconium the edge over stainless steel and titanium in HNO_3. Zirconium can also be the most cost-effective solution for solving nitric acid corrosion problems; longer equipment life, higher purity product streams, reduced maintenance and downtime can all be achieved with the proper use of zirconium.

LIMITATIONS

Despite the superiority of its corrosion resistance in HNO_3, zirconium is not suited for all nitric acid environments. As mentioned previously, stress corrosion cracking becomes a concern at HNO_3 concentrations above 70% or at 70% HNO_3 and elevated temperatures. This can be overcome with proper equipment design and heat treatment for stress relief.

Zirconium may also suffer pitting in the vapor phase of nitric acid and chloride mixtures. Chlorides could be oxidized to produce chlorine gas, which may induce pitting on zirconium. Giving zirconium a good surface finish, using methods such as pickling, can prevent this problem.

Finally, the presence of fluoride ions in a nitric acid solution can significantly increase the corrosion rate of zirconium.The fluoride ions tend to form undissociated hydrofluoric acid in HNO_3, with the corrosion rate of zirconium being directly proportional to the HF concentration. Adding an inhibitor to convert fluoride ions into non-corrosive complex ions can control this problem. Several compounds,including zirconium sponge and zirconium nitrate, can be used as inhibitors.

SAFETY

There is a special safety concern when using zirconium. Reactive metals like zirconium can develop pyrophoric films. Normally zirconium corrodes uniformly and all the zirconium is converted to zirconium oxide. If corrosion rates are low, <5 mpy,there is time to react all the zirconium uniformly. For very high corrosion rates, >200 mpy, the reaction rate is so high that all zirconium is also reacted.

At certain conditions,it is possible that the corrosion rate will attack grain boundaries and continue attacking the boundaries, trapping small pieces of Zr grains in the oxide and not completing the oxidation. Under these conditions, the oxide film may be pyrophoric. To passify the zirconium,the trapped zirconium pieces need to be completely oxidized before opening the equipment to air. This is achieved by passing hot air or steam through the equipment to make sure all the zirconium in the oxide film is reacted before opening to air. At 250C,air must flow for 20 minutes or steam for 30 minutes; at lower temperatures,several days of treatment are required.

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SUMMARY / CORROSION LAB SERVICES AND OTHER WAH CHANG RESOURCES

As demonstrated above, zirconium can be the best alternative for material selection in many nitric acid applications. Longer equipment life, reduced maintenance downtime, and higher purity product streams are all possible with the proper application of zirconium, making it the most cost-effective option when compared with other alloys.

Although, zirconium has proven its outstanding corrosion resistance performance in a wide variety of HNO_3 environments, the best way to determine zirconium 's suitability for a particular environment is to perform a corrosion test. Zirconium corrosion test kits are available from Wah Chang for use in on-line process equipment. These tests can show how zirconium will hold up under actual process conditions. Wah Chang also has a fully capable corrosion laboratory for complete testing and detailed analysis for specific nitric acid applications.

For further information or any questions regarding the use of zirconium in nitric acid applications,please contact the Technical Services Division at Wah Chang,phone 541-917-6777 fax 541-967-6987.

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