Titanium Valves for Hydrometallurgical Metal Extraction

Abstract
A major contributor to the successful operation of high-pressure acid leach (HPAL) operations has been the valves throughout the autoclave. The valve of choice has been the metal-seated floating ball valve. The corrosion resistance and strength of titanium has made it a key building material for equipment utilized in HPAL operations.

The objective of this paper is to provide knowledge about the design challenges for valves in PAL, the specific applications of those valves in PAL, and the specific materials in common use today.
Introduction

Acid leach processes have proven to be effective methods in the commercial extraction of nickel, gold, copper and cobalt from ore.

There are two primary processes used, pressure acid leach (PAL) and pressure oxidation (POX).

Both processes require the presence of sulfuric acid to leach the ore but the method of getting the acid is different. In the POX autoclave – typically used for gold and copper – the ore bodies contain sulfur so when water, heat and oxygen are added, sulfuric acid is produced in the autoclave. In the PAL process normally used to produce nickel, no sulphur is present so acid is injected into the autoclave.

A survey of HPAL plants in Western Australia in 2001 indicated that, “valve costs have represented 1 to 2 percent of the total new plant construction costs to date; however, their influence on productivity can be much greater. Maintenance costs for NiHPAL service are six times higher than originally anticipated; valve maintenance represents 30 to 40 percent of the total expense.”

Today, valve maintenance costs have been reduced and valves are much more dependable and reliable than in 2001. These improvements in efficiency have been achieved through advancements in design and material. Titanium has become the primary building block for piping, valving and autoclave in PAL and POX plants. The primary exception to this is that duplex stainless steel is used where the risk of oxygen auto ignition exists. In all cases, titanium is recognized as the material with superior corrosion resistant
properties. Oxygen injection valves in POX plants are typically duplex stainless steel because of the risk of auto ignition.

I. Characterization of PAL and POX Services

Temperatures at PAL plants typically operate at 550 F (260 C) with process designers desiring to advance to 550 F (288 C) and even 600 F (316 C). These temperatures prevent the use of soft sealing materials such as Teflon® or PEEK. Additionally, the elevated temperatures magnify the corrosiveness of the lading. Temperature also exerts thermal stresses at the coatings-base metal interface. Operating pressures in NiHPAL plants can exceed 700 psig.

Temperatures in POX plants are lower than in PAL with nominal autoclave operating pressures of around 450 psig (31 bar g) and temperatures less than 500 F (260 C).

Sulfuric acid concentrations in POX autoclaves vary from 15 to 25 grams/liter. In the PAL process, sulfuric acid is fed directly into the autoclave. PAL has typical acid concentrations of 45 to 65 grams/liter. In the POX process, oxygen is injected into the autoclave. This reacts with the sulfur in the ore and forms sulfuric acid. Processes chemistries are adjusted for ore content. This varies from site to site.

A raw ore body containing a reacted metal (nickel, gold, cobalt, etc.) is crushed and sized. This material is mixed with water forming a slurry paste. This slurry, initially at ambient temperature, is pumped into the autoclave. There, it is heated by the injection of steam to a temperature that, in the acid environment, converts the target metal into solution.

Metals in solution are recovered typically by two processes – electrolysis and precipitation. With metals in solution, the pH is gradually stepped up, precipitating the various reacted metals. Final extraction is made by an electroplating refining process.
Fig. 1, PAL Simplified P&ID

1. HP Heater Drain Valve
2. HP Heater Isolation Valve
3. Slurry Feed Pump Isolation Valve
4. Acid Valves
5. Drain Valves
6. Steam Supply Control Valve
7. Steam Valves
8. Vent Valves
9. Rapid Decompression Valve
10. Discharge Valves
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In summary, crushed solids transported through the system abrade, erode and damage the precision sealing surfaces of the valve ball and seats. Solids tend to
pack into clearances within the valve internals and prevent proper float of the sealing members, resulting in seat leakage and rapid erosive wear. Corrosion, due to the environment, can attack and deteriorate precision sealing resulting in spalling of the coating. Corrosion products can also expand to fill tight clearances in seats, again preventing proper float, resulting in seat leakage and rapid erosive wear. Corrosion can cause deterioration of the coating hardness and wear resistance.

II. Specialized Design Valving
Special designs and materials are used to manufacture valves for PAL and POX applications. These valves have evolved tremendously in the last 10 years. Successful designs have required the careful follow-up inspection and analysis of installed valves with design improvements continuously implemented to enhance performance. These valves must be robust, resistant to solids, resistant to solids packing in and manufactured of extremely corrosion resistant materials.

MOGAS discharge valves at the Ravensthorpe Nickel Plant
III. Materials

A. Material selection
The materials selected for construction of valves are determined by the following factors:

- Strength and mechanical property requirements – typically the responsibility of the valve manufacturer
- Application characteristics, pressure, temperature, corrosiveness – typically the responsibility of the end user

When valving is developed for specialized applications for which standard valving does not exist generally the best product is developed through a collaborative effort involving the end user and the valve manufacturer. This effort for MOGAS has included pilot plant testing, corrosion testing, field follow-up and performance analysis. In the case of wear resistant coatings, pure applied research was necessary to develop new coatings.
B. Titanium in use by MOGAS

1. Pure titanium – commercially pure titanium
   Grade 2
   Industry description
   “Grade 2 is a slightly higher strength unalloyed titanium that has led the way for titanium CPI applications. Its immunity to corrosion in most industrial applications along with its other attributes of good strength and ductility, shock resistance, fabricability, and weldability ensure that it will continue to be the most widely utilized grade. Grade 2 titanium is also the most readily available grade, offering substantial inventories of all mill products, including piping components.”

   MOGAS experience
   MOGAS has used grade 2 titanium for valve bodies in POX systems. These valves have performed very well with no reported problem.

2. Moderate strength – commercially pure titanium
   Grade 12
   Industry description
   “Grade 12 has been used for many years in equipment such as heat exchangers, piping, nozzles, shafting, and baffle plates. Many of these are identical applications as grade 2. One advantage grade 12 offers is a roughly 40 percent higher design allowable stress. This is due to the small alloying additions of nickel and molybdenum which allow for design advantages in terms of wall thickness, as well as providing for increased wear resistance. Grade 12 also offers enhanced corrosion resistance over grades 1 through 3, especially against localized corrosion. However, it does not offer the resistance of a palladium or ruthenium enhanced grade.”
MOGAS experience
Grade 12 titanium is currently the preferred titanium for valve bodies and piping in nickel PAL systems. The additional strength of grade 12 makes it suitable for some more highly stressed components such as balls. MOGAS valve bodies and balls constructed of this material have performed very well in field service.

3. High strength Alpha/Beta titanium
Grade 28 (Lean Alpha/Beta)

Industry description
“Grade 9 and 28 are titaniums that contain aluminum and vanadium, two of the most common alloying elements for titanium. Grade 28 has a ruthenium addition for enhanced corrosion resistance, analogous to palladium. Grades 9 and 28 have the benefit of strength through alloying while still retaining processing formability.”

MOGAS experience
MOGAS has utilized titanium grade 28 for higher strength applications including stems and springs. Grade 28 has a minimum yield strength of 70 KSI compared to a grade 12 minimum yield strength of 50 KSI. Components designed and manufactured of grade 28 have performed very well in service.

Grade 5 (Alpha/Beta)

Industry description
“Grade 5 is the most common titanium alloy, seeing an overwhelming percentage of use in the aerospace sector. It has been used sparingly in the industrial sector, including hydrometallurgy, for shaft, hub and impeller blade materials. The high strength of the material does, however, come at a price. The alloy is more prone to crack propagation than other, higher toughness, alloys. It can also be susceptible to SCC attack in aqueous chloride environments. It is the only titanium grade from Table 1 that displays reduced toughness in chloride environments.”

MOGAS experience
MOGAS has used grade 5 titanium in stems and springs. These components benefit from the high strength it offered by grade 5 (minimum yield strength of 120 KSI). Contrary to the industry
perception, MOGAS has seen no evidence of stress corrosion cracking in any grade 5 components including certain high chloride aqueous environments.

C. Wear resistant coatings
The wear resistant coatings utilized on the ball and seat sealing surfaces are specially developed ceramics. The performance of existing coatings was a major limiting factor in the life of PAL and POX valves. Early coatings were susceptible to both corrosion and rapid wear. Significant improvements have been made in nano-structured thermal spray. These improvements translate into extended valve life.

IV. Cost
Titanium is a relatively expensive material when compared to common carbon and alloy steels; however, it is important to consider the cost in light of its reduced density and long service life relative to other material possibilities. For example, a spot billet of titanium grade 12 may cost 15% more per/in$^3$ compared to a billet of Ferralium 255. The Ferralium has a much more limited anticipated service life than the titanium and is more difficult to repair. In most cases, the titanium valve will be the less costly to operate over a period of time and offers a superior value.

V. Machining
The majority of machine work is on the softer pure grades of titanium. Particulars are that titanium is somewhat gummy, tending to form long stringers. These stringers need to be routed away from the cutting point to prevent feed interruption. Feeds are faster and shallower somewhat like cutting aluminum. MOGAS manufacturing estimates titanium to require approximately 35 percent longer than 316SS to machine. Shop machinists prefer to machine titanium over duplex stainless steel. Tools used are either coated or uncoated carbide, and are selected to have very sharp edges. Machining of the stronger alpha-beta (grade 5) titanium is still reported to be manageable but slightly more difficult than the pure grades; feeds are reduced an additional 10 percent.

The expense of titanium means a shop’s scrap rate needs to be figured into the manufacturing costs. Depending on the shop’s skills, this can be a significant or insignificant expense.
References

1. Williams, John, George Kim and Jimmie Walker, “Ball valves with Nanostructured Titanium Oxide Coatings for High Pressure Acid Leach Service. Development to Application.”

Titanium Valves for Hydrometallurgical Metal Extraction

John Williams
Engineering Fellow
MOGAS Industries

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Overview

- What is hydrometallurgical metal extraction PAL, POX
- Specialized valving
- Materials used for valves
- Manufacturing valves of titanium
What is hydrometallurgical metal extraction?

- PAL — Pressure Acid Leach
- POX — Pressure Oxidation Leach

Macraes Gold in New Zealand

Porgera in Papua New Guinea
POX simplified P&ID
Ravensthorpe autoclave delivery
Slurry feed valves to autoclave
Characteristics of PAL and POX

- Corrosion
Characteristics of PAL and POX

- Erosion and wear
Specialized design valve
Specialized design valve

1. Stem
   Ti grade 12, 28,5

2. Body
   Ti grade 2,12

3. Spring
   Ti grade 12,5

4. Ball & Seats
   Ti grade 12, 5

5. Coating
   m and Titania, Chromia
Valve material of construction
Pure titanium

- Grade 2
Pure titanium

- Grade 2

Moderate strength pure titanium

- Grade 12
- Grade 28
Pure titanium
- Grade 2

Moderate strength pure titanium
- Grade 12
- Grade 28

High strength titanium
- Grade 5
Manufacturing

- Tools
- Speeds
Questions?

John Williams
Engineering Fellow
MOGAS Industries, Inc.
832-300-7846
jwilliams@mogas.com