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INTERNATIONAL MOLYBDENUM ASSOCIATION

# NEWSLETTER

JULY 2008

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## Obituaries

## Terry Adams

### Moly Market Guru

Terry Adams, who died aged 61 in a car crash in Sweden on 22 May, was the statistical guru of the moly industry.

After training periods with Rolls-Royce, British Steel and the Danish Atomic Energy Commission (DAEC), Terry Adams graduated in metallurgy in England in 1969. He returned to the DAEC as a research metallurgist for the next three years, primarily working on the development of zirconium alloys used for containment of enriched uranium pellets. After a brief period lecturing in metallurgy in the UK, he joined Noranda Sales Corporation of Canada, becoming involved with the commercial aspects of the company's production of molybdenum, fluorspar and uranium.

In 1980, he left a senior management post at Noranda to set up Adams Metals in Germany and England, to act as a molybdenum sales agent in central Europe for Codelco Chile, an appointment that continued until 1994. Since 1989, Adams Metals has also acted as the sales agents for Molymet, Chile for a variety of their molybdenum and rhenium products in several markets on both sides of the North Atlantic.

Over the years, Terry compiled a large molybdenum industry database which enabled Adams Metals to become a leading consultant in the industry. The company was a founder member in 1989 of the International Molybdenum Association.

Terry was unique as a speaker at IMOA AGMs and other conferences, in not only filling the conference room but also keeping the audience awake with his analyses of supply and demand and his mind-blowing graphs and arrays of figures. His expertise will be greatly missed by the Association.

Terry is survived by his daughter, Nicole, and his son Paul. They will continue to run the family business of Adams Metals.

## Luis Casali

### Rising Star at Molymet

Too young yet to have become a guru, but already having made his mark on the industry, Luis Casali was travelling with Terry and died at the age of 35 in the same tragic accident.

Luis received a degree in Economics and Administration (Commercial Engineering in Chile) from the Universidad Finis Terra in Santiago. He joined Molymet in 1998, where he began a successful executive career in different areas, such as Logistics, Finance and Sales.

He moved from Santiago to London with his family in February 2006, as a member of the team which set up Molymet Services, an affiliate Company to Molymet. Highly regarded, he was appointed Sales Manager of Molymet Services and was responsible for sales of Molymet products in the European and Asian markets.

Luis had a great sense of humour and liked sports, having distinguished himself both in rugby and football. He had many friends in Chile and in England.

Luis is survived by his wife, Alejandra, and their young children, Franco and Augusta.

***All of us at IMOA who knew Terry and Luis extend to their families, friends and colleagues our deepest sympathy.***

# Lean Duplex Stainless Steel Flexible Flowlines for the Kikeh Offshore Oil Field

***This is a condensed version of the paper "AL 2003 (S32003) Lean Duplex Case Study: Flexible Flowlines for an Offshore Oil Field Development", presented by John Dunn at Stainless Steel World 2007, Maastricht, The Netherlands, November 8, 2007, edited by Dr. Gary Carinci, TMR Stainless, Pittsburgh, PA, Consultant to IMOA***

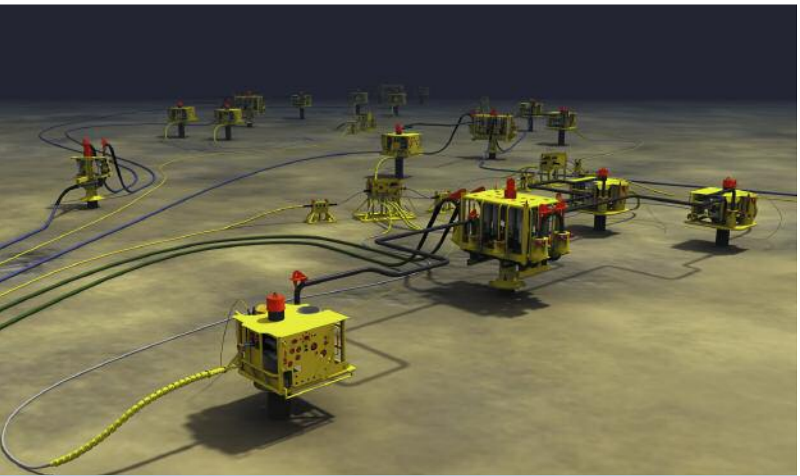


***Figure 1:*** *Kikeh subsea production system consisting of 16 " christmas trees", 5 manifolds, 21km of flowliness and umbilicals. Image courtesy of Aker Kvaerner.*

## Introduction

Unbonded flexible pipe has been successfully used throughout the world to transport produced fluids from subsea oil and gas fields. Flexible pipe is extremely well suited for use in conjunction with Floating Production Storage Offloading (FPSO) vessels due to its ability to accommodate the dynamic nature of their positioning systems. FPSO has emerged as one of the leading topside technologies and is being used for new fields such as Kikeh, offshore of Sabah, Malaysia ***(Figure 1)***.

For flexible pipe carcass, the corrosion performance of the stainless steel is critical to the performance of the pipe as a whole. It must be carefully characterized in order to allow an accurate and confident material selection during pipe design. Recent and future applications of floating production systems are increasingly in more severe environments. They include design temperatures up to 145°C (293°F), design pressures from 345 to 690 bar (5,000 to 10,000 psi), sour production fluids, water depths exceeding 2,000 m (6,561 ft), and severe ocean wave and current conditions.[1,2] Flexible pipe typically employs polymer and carbon steel materials, extruded and helically wound around the inner stainless steel carcass, to give axial, hoop and tensile stress reinforcement ***(Figure 2)***.

As flexible pipes are used in deeper water, pipe weight increases, resulting in higher deck and installation loads. Hydrostatic pressure from the external weight of water must also be resisted to prevent collapse of the pipe structure. The carcass supports the polymer fluid barrier, preventing collapse, so higher strength material is therefore required in the carcass for deep-water applications. Duplex stainless steels have been employed for carcass material to reduce pipe weight and improve collapse resistance, due to their high strength, compared with conventional 300 series austenitic stainless steels ***(Table 1)***.

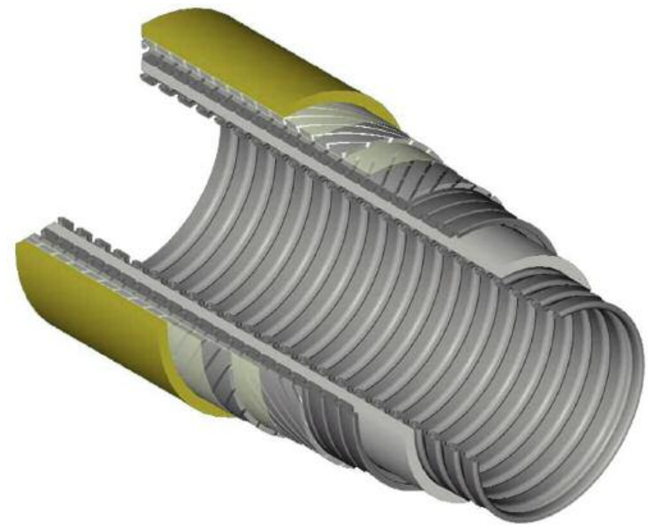
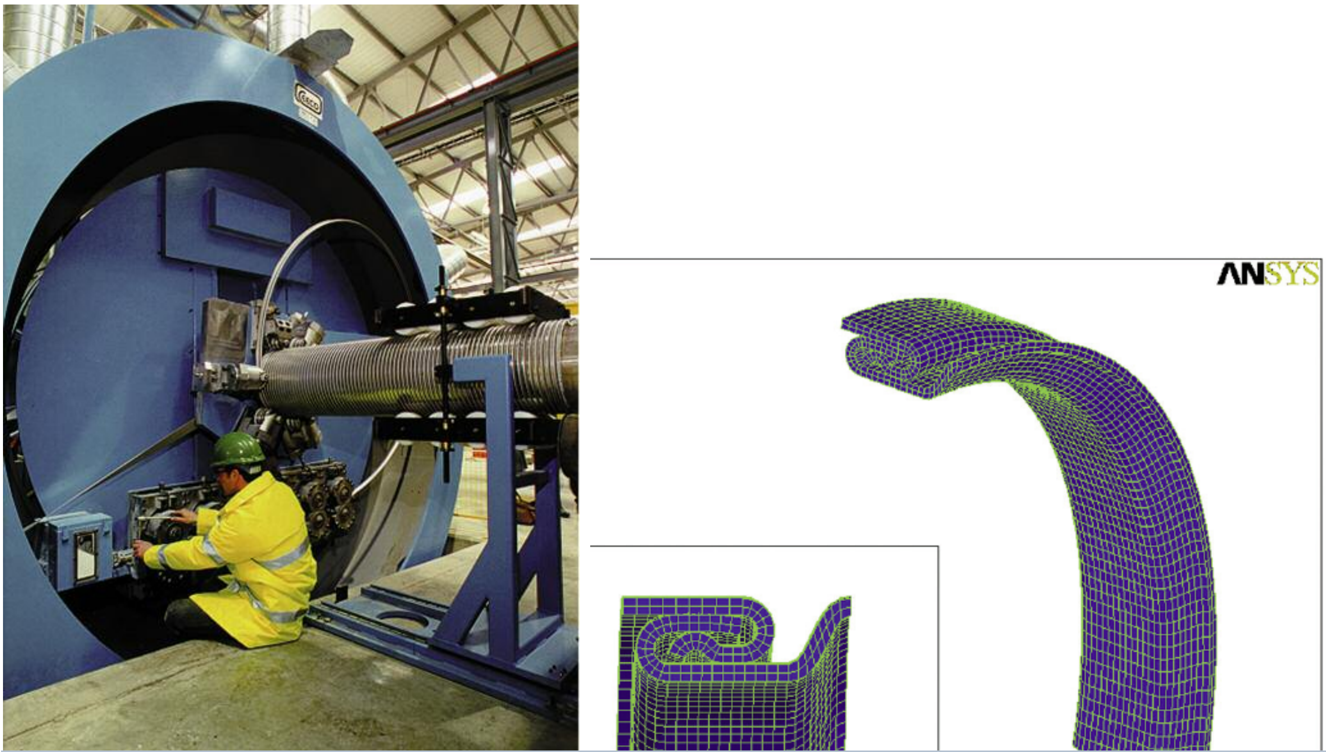


***Figure 2:*** *Flexible pipe cross section showing inner carcass layer: image courtesy of Wellstream International Ltd.*

***Table 1.***
*Mechanical properties, chemical composition (wt%), and PREN comparisons.*

| Group | Grade UNS | Yield (MPa) | Tensile (MPa) | Cr | Ni | Mo | N | PREN |
|---|---|---|---|---|---|---|---|---|
| Austenitic | S31603 | 170 | 485 | 18.2 | 10 | **2.2** | - | 24 |
| Lean Duplex | S32003 | 450 | 620 | 21.5 | 3.5 | **1.8** | 0.16 | 30 |
| Duplex | S32205 | 450 | 655 | 22.5 | 5.5 | **3.3** | 0.16 | 36 |

PREN = %Cr + 3.3%Mo + 16%N




***Figures 3 and 4:*** *Strip forming into pipe with cross profile of s-interlock.*

At 1,400 m (4,600 ft) water depth, the Kikeh field was too deep for Type 316L carcass material, and the molybdenum-bearing Lean Duplex Stainless Steel (LDSS) 2003 (UNS S32003) was of particular interest as a replacement candidate for Type 316L (UNS S31603). The S32003 LDSS is a lower cost alternative to 2205 (UNS S32205), a standard 22% Cr Duplex Stainless Steel (DSS). J. Dunn et al[3] discuss the Kikeh Field application using S32003 in detail, and this article summarizes their published work.

Extensive qualification in accordance with American Petroleum Institute (API) 17J was completed by Wellstream International Ltd. to confidently and cost effectively design with S32003 instead of using 316L or 2205 stainless steel[4]. The qualification program and the Kikeh field conditions are discussed below.

## Kikeh Field Conditions

Kikeh is considered the first deepwater development of its kind in the Asia – Pacific region, utilizing a floating drilling platform and production in conjunction with an FPSO.[5] Recoverable reserves are put at more than 400 million barrels of oil.[5] The field was discovered in August 2003, started production in August, 2007 and will ramp up to 120,000 barrels of oil per day through 2008. Total project capital expenditure was estimated at $1.4 billion (U.S.). [6]

The subsea production system involved 21 km (13 miles) of flowlines and umbilicals, and more than 15 km (9.3 miles) or 545 metric tons utilized lean duplex S32003 for the carcass material. The flowlines consisted of oil production, gas export and seawater injection lines.

## Material and Manufacturing Considerations

Carcass material considerations include strength, corrosion resistance of the formed strip and welds, erosion resistance, and collapse resistance. ***Figure 2*** illustrates the inner carcass layer encased by additional layers of carbon steel and polymer. To manufacture the carcass, flat strip is formed into an S-profile, which is then interlocked to form a flexible pipe as illustrated in ***Figure 3 and 4***. The carcass tube is reeled before the remaining layers of carbon steel and plastic are constructed over the carcass. The finished pipe is packaged and shipped to the field for installation where it is unreeled on the vessel and then laid in position on the seabed.

For the Kikeh project, carcass material comparisons were performed as follows:

### Corrosion Resistance

***Table 1*** shows the alloy comparisons for 316L, S32003, and 2205 stainless steel. The Kikeh field required a level of corrosion resistance at least equal to 316L

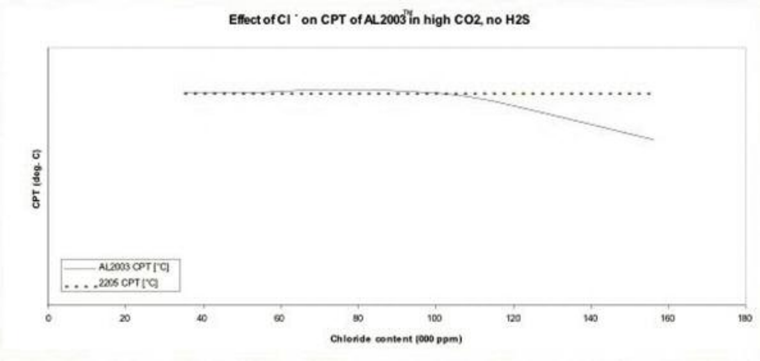



***Figure 5:*** *Modified ASTM G150 Critical Pitting Temperature comparison*

in the as-welded condition (strip to strip welds are required in order to form long lengths of pipe). Based on the chemical composition, the Pitting Resistance Equivalence Number (PREN) predicts that S32003 has higher pitting resistance, calculated at 30, compared with 316L at 24. The higher pitting resistance of S32003 was confirmed by corrosion testing Gas Metal Arc Welds (GMAW), produced with 2209 wire on plate samples by Allegheny Ludlum, through ferric chloride testing in accordance with ASTM G48A.
The as-welded S32003 had a Critical Pitting Temperature (CPT) in excess of 10°C, compared to 316L at 0°C.[7,8] Formed S32003 strip and strip-weld samples were also tested using ASTM G48A and in accordance with ASTM G150, modified with $CO_2$ in an autoclave, and little difference was found in CPT up to 100,000 ppm chlorides when compared to 2205 ***(Figure 5)***[9].

## Strength

Weld properties were also examined for impact strength at low temperatures. In comparison to the acceptance criteria established by ASTM A923 and Norsok M-630, S32003 GMAW, welds in plate samples exceeded the requirement as shown in Table 2.[10,11,12] These results are worst case values for testing of the weld zone (2209 filler), fusion line and heat affected zone.

The ASME allowable design strength ***(Figure 6)*** also shows a distinct advantage for S32003 and 2205 compared to 316L.[13] This advantage could contribute to wall reductions for pressure vessels or pipe, and improvement in collapse resistance for deep-water applications.

## Collapse Resistance

Collapse tests were performed on the unbonded flexible pipe prototype with various carcass materials and representative installation crushing loads were simulated. At a depth of 1400 m, the Kikeh field was too deep for 316L carcass consideration as illustrated in ***Figure** 7*. This figure shows predictions for straight collapse, and indicates that even pipes with a duplex stainless steel carcass are challenged at this water depth with increasing pipe diameters. However, large diameter water injection lines have the benefit of having internal water pressure to combat the external hydrostatic head of seawater. In reality they, therefore, have to withstand only the pressure difference between the outside and the inside. The predicted collapse results clearly show the benefit from the selection of S32003 compared to 316L pipe. The predicted collapse resistance falls between that of 316L and 2205 stainless steel.

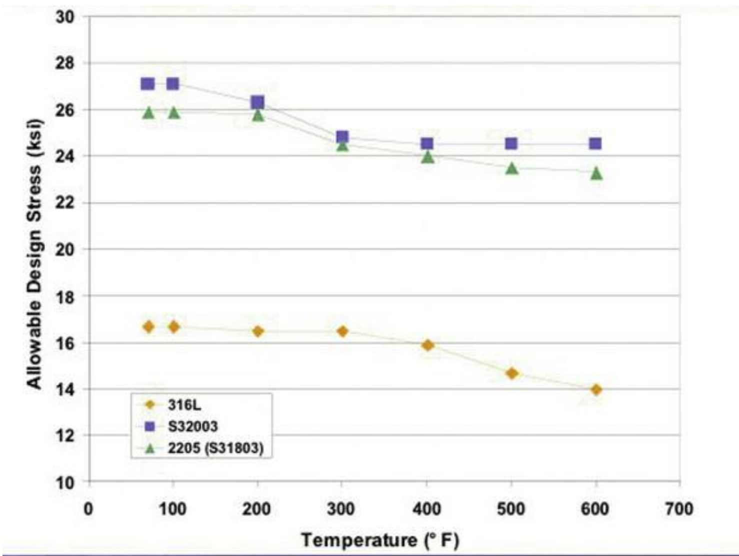



***Figure 6:*** *ASME design strength comparisons.*

***Table 2**. Impact properties comparison of 316L and S32003 stainless steel.*

| Sample/Criteria | -46°C (-51°F) | -40°C (-40°F) | Room Temp. |
|---|---|---|---|
| 316L Base | N/A | 210 J (155 ft-lbs) | 190 J (140 ft-lbs) |
| 316L Weld | N/A | 100 J (75 ft-lbs) | 110 J (80 ft-lbs) |
| S32003 Base | 110 J (80 ft-lbs) | 135 J (100 ft-lbs) | 245 J (180 ft-lbs) |
| S32003 Weld | 70 J (50 ft-lbs) | 80 J (60 ft-lbs) | 200 J (150 ft-lbs) |
| Norsok/ASTM Criteria | 45 J average<br>35 J individual | 55 J min. | |

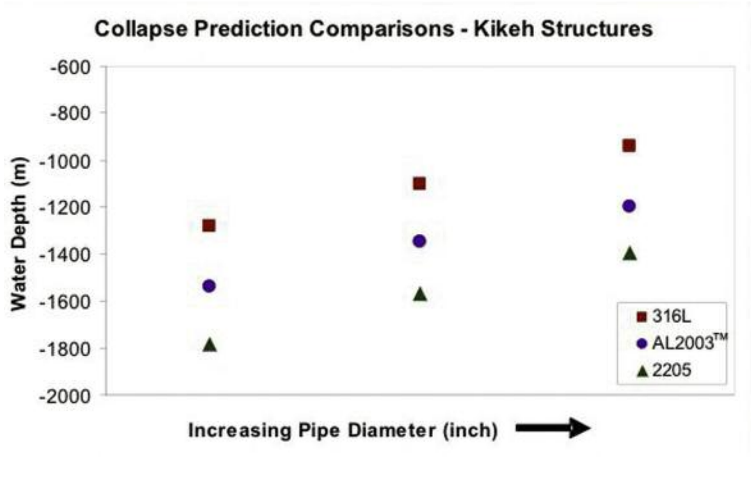



*Figure 7: Collapse resistance of unbonded flexible pipe with different carcass materials.*

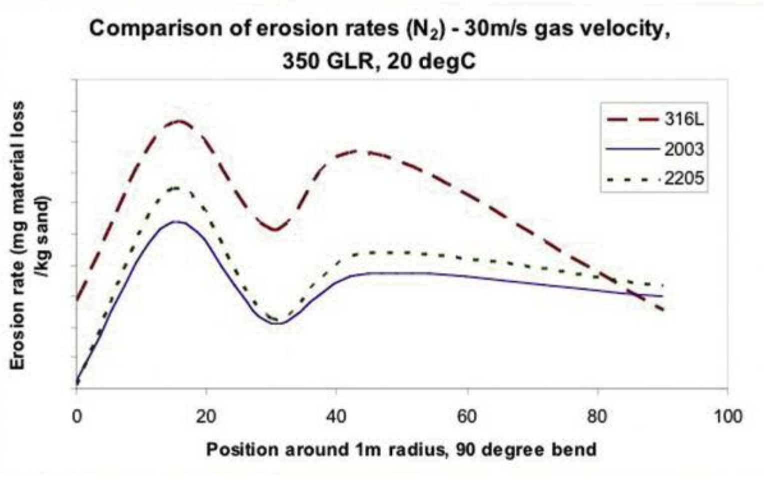



*Figure 8: Comparison of erosion rates for 316L, S32003 alloy and 22%Cr DSS.*

## Erosion Resistance

Erosion and erosion-corrosion can be a concern for flowlines in fields where there is high sand intake or high flow velocities. This can be compounded by some of the elements being transported with the production fluids (oil, water, and corrosive gasses). Several carcass-only prototypes with 316L, S32003 and 2205 were manufactured by Wellstream in order to compare their erosion-corrosion resistance in simulated flow conditions. At high fluid velocities and high Gas/Liquid Ratios (GLR) ***(Figure 8)***, results showed similar performance for S32003 and 2205, but 316L samples had substantially higher erosion rates. However, at lower gas velocities and/or reduced GLR or increased temperatures, no significant differences in erosion-corrosion rates were apparent between the three grades.

## Conclusions

A new Lean Duplex Stainless Steel S32003 was used in the flexible flowlines for the Kikeh deepwater subsea oil and gas project. The S32003 carcass was selected due to its combination of corrosion resistance and strength. More than 15 km of unbonded flexible pipe with S32003 carcass has already been installed.
This material met or exceeded 316L stainless steel properties in all qualification testing. S32003 is considered an improved alternative to 316L carcass in unbonded flexible pipe, and an economic alternative to 2205 unbonded flexible pipe in some field conditions.

## References: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2. J. Tuohy, A. Avery, S. Martin, “Unbonded Flexible Pipe Technology in Deepwater Developments for Production and Offloading Systems”, OWA 2001, Abuja, Nigeria, 21-23 March 2001.

3. J. Dunn, D. Hasek A. Cameron, R. Clements, “AL 2003™ (S32003) Lean Duplex Case Study: Flexible Flowlines for an Offshore Oil Field Development”, Stainless Steel World 2007, Maastricht, Netherlands, November 8, 2007

4. American Petroleum Institute Specification API 17J: Specification For Unbonded Flexible Pipe.

5. J. Maksoud, “Malaysia’s field of ‘firsts’”, Offshore, April 2007, pg 92-96.

6. K. Evensen, A. Battersby, “Smedvig in Clover with Kikeh Deal”, Upstream, 4 March 2005, pg. 33.

7. ASTM G48: Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution: Method A.

8. “AL 2003 (S32003) Weld Procedures and Evaluation”, Allegheny Ludlum Technical Publication, 2005.

9. ASTM G150: Standard Test Method for Electrochemical Critical Pitting Temperature Testing of Stainless Steels

10. ASTM A923: Standard Test Methods for Detecting Detrimental Intermetallic Phase in Duplex Austenitic/Ferritic Stainless Steels.

11. Norsok M-630: Material data sheets for piping (Rev. 4, January 2004)

12. J. Dunn, D. Bergstrom, “AL 2003 (S32003) Lean Duplex Stainless Steel as a Substitute for Type 316L”, SSW, November 2006.

13. J. Grubb, “A Lean Duplex Stainless Alloy for Pressure Vessel Applications - ASMECode Case 2503”, Outlook, March 2006, Vol 27, pg. 12-13.

# Super Duplex Stainless Steel for Extended Service Life

*IMOA Consultant John Grocki wrote this case study with background information provided by George Furmanski, Senior Project Engineer, CalEnergy Operating Company.*

## SUMMARY

CalEnergy has been operating in the Salton Sea geothermal area since 1971 and generating geothermal electric power since 1980. At present CalEnergy has nine multi-loop flash/steam power plants generating 380 MW. It plans to add three additional plants (approximately 50 MW each) to reach 540 MW by 2015.

A test program utilizing 2507 (S32750) pipe, tees and elbows was started in 2005. After several evaluation periods, it was determined that this material would provide an approximate 15-year life at a significant savings when compared to the nickel alloy. An initial order for 800 metric tons of 2507 pipe and fittings was placed in 2006. A second order of similar size was placed in 2007. The combined requirements amount to approximately 5800m (19000') of 610mm (24") diameter pipe and 9150m (30000') of 760mm (30") diameter pipe. Additional orders are planned to complete the updating projects by 2011 and to support the additional new plants whose construction will start in 2011.

**Figure 1:** *CalEnergy Leathers Plant, Calipatria, CA*

CalEnergy has had an ongoing brine delivery pipe development program since the early 1980s. Originally carbon steel was used for the pipeline delivering the hot brine from the wellhead to the plant. The carbon steel pipe had a life of one to two years and, by mortar lining the steel pipe, the life could be extended to two to five years. In the late 1980s CalEnergy installed nickel alloy 625 pipe and that provided service life in excess of 18 years. Because the cost of the nickel alloy pipe was prohibitive when considering the extent of the planned rebuild and new build projects, an alternate material with a reasonable life expectancy was required. Alloy 2205 (S32205) was tried first as a liner material and later as a solid pipe material. The 2205 gave mixed results and stress corrosion cracking and localized corrosion was a concern.

## THE PROCESS

The delivery pipeline brings the geothermal brine from the wellhead to the plant where it is flashed to vapors,*(Figure 2)* which are used to drive a turbine, which in turn drives a generator and produces energy. Generally, the brine is delivered at 260°C (500°F), 42bar (600 PSIG), contains 130 to 160,000 ppm of chlorides, 800 to 5000 ppm $CO_2$, 80 to120 ppm H2S and has a total dissolved solids content of 250 to 310,000 ppm. In today's process, the brine is acidified inside the plant from its normal pH 6.0 to a pH of 4.8 to 5.0.

## THE CORROSION

Considering the high chloride levels coupled with the high temperature and moderately acid pH, it is obvious that pitting corrosion must be considered for both the base material and more particularly the weld zones. With the high solids content, scale formation and other deposits in any flow-affected areas provide the potential for aggressive crevice corrosion. In addition, any stressed areas such as weld zones, movement restricted locations or heavily cold-formed areas could be considered sites for chloride stress corrosion cracking CSCC.

## THE TEST PROGRAM

In 2003, a test pipeline over 2205 was installed to handle acidified brine at 205°C (400° F) and 8.5bar (125 PSIG). In December 2005, the 2205 pipeline

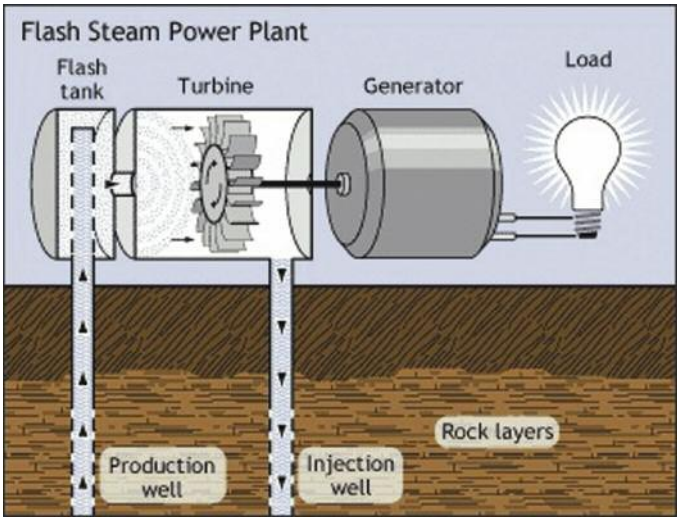


**Figure 2:**

*Schematic of a flash steam power plant: Hydrothermal fluids above 182°C (360°F) can be used in flash plants to make electricity. Fluid is sprayed into a tank held at a much lower pressure than the fluid, causing some of the fluid to rapidly vaporize, or "flash." The vapor then drives a turbine, which drives a generator. If any liquid remains in the tank, it can be flashed again in a second tank to extract even more energy.*

*(Source:http://www1.eere.energy.gov/geothermal/powerplants.html)*

was evaluated. While there seemed to be no localized corrosion occurring on the base metal wall thickness, readings showed values down to 10.9mm (.429in) from the original 12.7mm (.500in). In addition, 7 of 48 weld joints showed ID crack indications and one weld was actually leaking.*(Figure 3)*.

In April 2005, a test spool of 2507 pipe (welded with Inconel 686 CPT filler metal), tees and elbows was installed to handle the 260°C (500°F), 42bar (600 PSIG) non-acidified brine. The initial evaluation after 13 months of service, and a second evaluation after 20 months, showed no degradation of either the base metal or the weld zones. The last evaluation after 24 months revealed some minor pitting and possible CSCC in one weld zone. The pitting occurred at two locations geometrically opposed in the elbow and it is probable that the pits are the result of surface damage occurring during fabrication or transportation. The CSCC occurred parallel to the weld and no abnormal metallurgical conditions were observed in that area. Excessively high stresses resulting from the weld procedure are certainly a contributing factor. Weld procedures for joining pipeline segments will be specifically developed and implemented in a way to minimize resultant stresses and, therefore, the potential for CSCC.

***Figure 3:***
*Salt buildup from the evaporated brine at leak sites in 2205 duplex stainless steel pipes.*

***Figure 4:***
*The field welding is carried out in a controlled environment in a tent.*

## THE SOLUTION

Based on these evaluations it was determined that the highly alloyed duplex stainless steel 2507 (25Cr 7Ni 3.5Mo) has adequate corrosion resistance in geothermal brine to provide an approximate 15 year service life with the potential for minimal required maintenance. In addition to developing specific field welding procedures, the over alloyed Inconel 686CPT (58.5Ni 20.5Cr 16.25Mo 4W) filler metal was chosen to ensure corrosion resistant pipe section joints. *(Figure 4)*.

## THE COST SAVINGS

The 15 year life with minimal maintenance can certainly be seen as a cost effective measure when compared to replacing carbon steel, even mortar lined, every 2+ years.Further, the initial cost difference of the duplex stainless steel pipeline is expected to be approximately 25% to 35% less than that for a similar pipeline constructed from the nickel alloy tested.

***Table 1**: Nominal Chemistry of Materials*

| Trade name | Standard | | Chemical composition (weight %) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | UNS | EN | C | Cr | Ni | Mo | N | W | Fe |
| 2507 | S32750 | 1.4410 | <0,03 | 25 | 6,5 | 3,6 | 0,26 | - | bal |
| 2205 | S31083 | 1.4462 | <0,03 | 22 | 5 | 2,8 | 0,16 | - | bal |
| | S32205 | | | 22,5 | 6 | 3,3 | 0,18 | | |
| 686 | N06686 | 2.4606 | <0,03 | 21 | 58 | 16,3 | - | 3,8 | 1,5 |
| 625 | N06625 | 2.4856 | <0,03 | 22 | 60 | 9 | - | - | - |

***Table 2:** Supplier References:*

**UNS S32750 plate** - ArcelorMittal Industeel, Belgium
**Pipe Products** - Butting GmbH, Germany
**Fittings** - EZEFlow, Inc., Canada
**Filler Metal** - Special Metals Corp., USA
**Field Welding** - Carolina Energy Solutions, USA
**Inspections** - Stork Metallurgical Testing & Inspection, USA

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