



Langley Alloys

Super-Duplex

Ferralium® 255 for FGD Applications

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Gibson Station is now Duke Energy's largest power plant. It is a five-unit facility that was built between 1976 and 1982. Unit 5 is co-owned by Wabash Valley Power Association and Indiana Municipal Power Agency. All five units have sulfur dioxide scrubbers.



Drax Power Station is the largest generating station in the UK. Pollution control systems are installed in all units, although the station has been partially converted to use biomass instead of coal.

Reliable resistance to corrosion

Pollution control systems are now required on a diverse range of industrial processes to reduce gaseous and liquid emissions to an environmentally acceptable level. In particular, sulphur gas emissions are controlled by FGD systems on coal burning power plant. Ferralium® 255 – 25%Cr (Cu+N) duplex stainless steel – has been selected for use in 'gas path' and liquid/slurry areas of FGD plant. Long term success with the alloy at PSI Energy, USA, is described in detail.

The reduction of gaseous and liquid emissions from an increasingly diverse range of industrial plant is being sought in many countries. One prime source of aerial emissions is fossil fuel burning power stations, and member countries of the EC are participating in a programme to reduce such pollution following the adoption of the Large Combustion Plant Directive in the late 1980's. Flue Gas Desulphurisation (FGD) to reduce sulphur emissions is being applied in the EC to follow what has been practised in Germany, USA and Japan for a number of years. The operating conditions for equipment to control pollution can be extremely arduous and cost effective material choices need to be made to provide equipment which can run for long periods without costly maintenance, and allow operators to meet their obligations under legislation by virtually continuous operation. Duplex stainless steel can provide an extremely effective solution to material selection for the vessels, fans, mixers, pumps, valves and centrifuges, which are often required to handle acid conditions contaminated with chloride and to withstand quite severely abrasive and erosive slurries. An attractive life cycle cost is available compared with lined carbon steel, austenitic stainless steels and high nickel and nickel-base alloys.

Duplex stainless steels

Duplex stainless steels, like austenitic stainless steel, is not a unique material, but comprises a range of alloys of various compositions, but all containing roughly 50% of austenite dispersed as islands in a ferrite matrix. The ferrite matrix imparts high strength and erosion resistance, the austenite impacts ductility, and the duplex structure is beneficial to

weldability compared with fully ferritic or fully austenitic steels. The corrosion resistance depends on the composition and also on the partitioning of the elements between the two phases. In general, the elements chromium and molybdenum are enriched in the austenite phase.

It is accepted that chromium, molybdenum and nitrogen increase the resistance to pitting in seawater. In more critical conditions, additions of copper provide major improvements to both corrosion and erosion resistance. Thus crevice corrosion tests carried out for the US Navy on a large number of nickel-base alloys and stainless steels about 10 years ago indicated that copper was beneficial in reducing the breakdown of oxide films in Ferralium® 255 duplex steel⁽¹⁾.

Pini and Weber⁽²⁾ reported much superior erosion and corrosion resistance in high-velocity seawater containing H₂S in copper-containing duplex steels and copper-containing 13% chromium ferritic steels compared with the copper-free equivalents and considered that copper and molybdenum acted synergistically (Table 1). Simpson⁽³⁾, also of Sulzer, demonstrated synergy between copper and nitrogen in promoting corrosion resistance of duplex steel in sulphuric acid, of direct relevance for pollution control and FGD applications in particular.

Alloy	Relative loss of material
Duplex steels containing copper	30 - 400
Copper-free duplex steels	6,000 - 7,000
13% Cr steels	30,000 - 50,000
13% steels containing copper	600 - 700

Table 1. Effect of H₂S contamination on corrosion of copper-containing and copper-free duplex steels and 13% Cr steels - relative loss of material in media containing H₂S (pH 5.5, T = 50°C, velocity = 50m/s).

The effects of copper in improving the strength and hardness of duplex steels and also their corrosion and erosion resistance in sulphuric acid slurries are substantiated in actual service, so that Sulzer have found it convenient to define environments in FGD plant into distinct categories in which copper-free duplex steels would be adequate, or in which it would be advisable to use copper-containing 25%Cr duplex steels such as Ferralium® 255 for pump bodies. For pH above 4 and chloride content below 30,000 ppm copper-free duplex is employed, whereas for more acidic, pH 2.5 to 4, and chloride content in the range 30,000 to 40,000 ppm copper-containing duplex steels are employed. Duplex stainless steel containing a substantial addition of copper has also been found to resist corrosion attack by hot dilute hydrochloric acid more successfully than low copper duplex materials ⁽⁴⁾.

Experience with Ferralium 255

Ferralium® 255 has been used with notable success for the retrofit lining ¼" thick, of horizontal absorber vessels at Gibson Generating Station of PSI Energy, Indiana, USA. Gibson unit #5 burns 3.4% sulphur bituminous coal. A wet magnesium enhanced limestone flue gas scrubber built to reduce SO₂ emissions at the stack outlet to comply with federal regulations. This unit went into operation in October 1982 with carbon steel absorber vessels lined with an inorganic calcium-alumino-silicate gunite-type lining, reinforced with a carbon steel wire mesh. Cracking and erosion of the lining resulted in the decision to replace the lining, and after an economic evaluation ⁽⁵⁾ it was decided to install a metal alloy liner.

Ferralium® 255 was chosen on the basis of its mechanical properties, corrosion resistance and cost after testing of various alloys in corrosion racks in an absorber at the Gibson station (see Table 2 for the absorber slurry chemistry) and assessment of a set of mist eliminator supports fabricated in the alloy and placed in service in 1983. These supports looked 'as new' after 3 years with no sign of pitting or erosion. The 25%Cr super duplex alloy plates were butt welded together using an SMAW process and attached by plug welds through the carbon steel vessel. The same alloy was used in pipe form to line the nozzle sleeves (144 off, 150mm diameter) where the spray nozzles penetrate the absorber roof.

Total suspended solids	1.4 – 2.0%
pH	5.3 – 5.5
Calcium	200 - 400ppm
Magnesium	6,000 – 8,000ppm
Sulphite	2,000 – 4,000ppm
Sulphate	10,000 – 20,000ppm
Chloride	3,000 – 12,000ppm
Thiosulphate	1,500 – 2,500ppm

Table 2. The absorber slurry chemistry.

During the same shutdown, the FGD vendor was completing some needed design modifications. It was necessary for the vendor to add another stage of mist elimination to each absorber. Because of the limited space available, the vendor designed a multi-purpose box member. This member supported the first-stage mist eliminator and the wash spray headers for the second-stage mist eliminators. The top sections of some members acted as supply headers to individual mist eliminator wash spray headers, while the lower half of some members acted as drain headers for the first-

stage mist eliminator upper sections. The vendor decided to use Ferralium® 255 for this fabrication based on the reasons listed earlier. The box member was fabricated by bending plates into 90 degree angles and then welding two angles along their entire length to form the box. Ferralium 255 studs and brackets were then attached as required to complete the assembly.

After trouble free installation in autumn in 1986 of the lining (2,600m²) and mist eliminators the high alloy duplex material has been in service for six years. The general appearance of the lining and welds is reported by PSI Energy to be essentially the same as the day it was installed ⁽⁶⁾. There has been no noticeable erosion damage of the lining or welds in the slurry impact zones on the side walls or downstream surfaces of the drain troughs. There has been some concern that the duplex alloy might not be a viable long-term for the wet-dry interface at the absorber inlet where the 300°F (149°C) flue gas meets the first spray zone and high chlorides are present. The performance of the copper-containing duplex steel has been such that the initial concept of 'wall papering' this area with Alloy C276 after one or two years' service was abandoned. After 3 years' service some shallow pitting (0.4mm depth) was found, but after 5 years this depth had not increased significantly and the duplex steel is still performing well.

There was also some initial concern about the box members. Where the Ferralium® 255 was in contact with the carbon steel press brake, carbon steel had been smeared into the surface during forming the 90 degree angles. Almost immediately after being placed in service, a rust strip was prominent on each face of the box member. There was concern that this would set up active corrosion sites. During the first years inspection it was noticed that all the carbon steel had dissolved with no apparent effect on the Ferralium® 255. After six years there is no sign of corrosion or erosion of the box members.

PSI Energy have a policy to use Ferralium® 255 as the prime material of construction for future FGD absorbers and the alloy is being employed for the construction of a new unit in 1992. At the same time the high copper duplex has been used to construct dampers for outlet ducts by butt welding 1" thick plate. Big River Electric Corporation, Sabree, Kentucky, USA, have used Ferralium® 255 to line guillotine dampers in the outlet ductwork and the floor area of the outlet ducts adjacent to the bypass reheat duct area. In these areas where the conditions were reported as pH 1 to 2, Cl- 1,000 to 3,000ppm and temperature 125degF the alloy has performed without problems for over 5 years ⁽⁷⁾.

For Drax Power Station, operated by National Power UK, where high chlorine content coal is usually burned, equipment such as pumps, valves, centrifuges and mixers will operate in corrosive/erosive conditions with a temperature of 50-60°C, pH 4.5 to 6 and 30,000-40,000ppm Cl-. Alloy 2205 stainless steel was not best suited to this corrosive/abrasive environment, hence cast and wrought Ferralium® 255 was used for the production of pumps, valves, side entry mixers, absorber spray nozzle bolting and gas distribution plates. Ratcliffe Power Station, operated by Powergen UK, will also employ 25%Cr duplex steel for pumps, valves, centrifuge baskets and side entry mixers. In Germany, pumps and valves in 25% Cr duplex (Cu+N containing) have been widely used with success. For example, Sulzer Pumps have supplied many pumps to REA, Voerde, in this duplex steel composition.

Conclusions

- 25%Cr duplex stainless steels (with Cu+N) have an important role to play in the production of cost effective equipment for FGD and other pollution control systems.
- The corrosion/erosion resistance and mechanical strength of Ferralium® 255 make it ideally suited to equipment produced from castings and all wrought forms where reliable resistance to pitting, crevice, stress and acid-corrosion is required.

References:

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Post-script:

Although the original article was published in 1992 (Stainless Steel Europe, November issue), meaning that references to both legislation and customers are now dated, the fundamental analysis, product selection criteria and end-user experience are still relevant.

The demand for FGD pollution control systems dramatically fell away as legislation favoured investment in alternative energy sources, be that gas-fired instead of coal-fired generation or latterly renewables (solar photovoltaic, wind). In the case of the Drax power station, it has been partly converted to the burning of sustainable biomass. However, changes in the political environment in certain countries means that limited development of coal-fired stations will persist, usually with FGD systems as a mandatory requirement.

Significant development of alloys for FGD applications continued through the 1990's-2000's, driven by the desire to improve corrosion performance and/or reduce initial investment costs. Therefore, there are now even more choices than before, with a variety of lean duplex alloys available in addition to super duplex and super austenitic alloys.

More recently, similar approaches to pollution control are being implemented for marine vessels. Typically seawater is used as the process medium, rather than a 'limestone slurry', but equally corrosive chloride-rich conditions exist. The superior corrosion resistance of super duplex alloys, such as Ferralium® 255, make it eminently suitable. As current legislation allows vessels to sail without pollution control systems in operation when outside sensitive regions, the units can experience temperatures above the sensible range for super duplex alloys, so austenitic and super austenitic alloys are presently favoured. Ferralium® 255 is still widely utilised in pumps and valves, and can offer enhanced performance in units that operate continuously and/or when legislation changes to require low emissions irrespective of location.

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