Stainless Steel Converter Performance

11 Years Later

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Summary

In 1984 the writer presented a paper a the Clearwater Convention of AIChE. The subject was the installation of the Chemetics' stainless steel converter at Essex Chemical, Newark, N.J. This years' paper is in two parts; the first discusses the progress of the Chemetics' stainless steel converter which "11 years later" has become the preferred converter design concept for modern sulphuric acid plants.

The second part of the paper describes in detail the "flaking" phenomenon which has recently received exaggerated reports as a problem associated with stainless steel converters.

Chemetics Converter Experience

Since 1981 Chemetics has sold 22 stainless steel converters. Applications have been split as follows:

- *metallurgical (11 off);*
- *regeneration (3 off; and*
- *sulphur burning (8 off).*

Countries where these units have been sold include Canada, USA, Australia, UK, Belgium, Peru, China, Kazakhastan and The Netherlands. Designs have been 1, 3 and 4 bed units with diameters ranging from 16 ft. to 46 ft. See photograph No. 1.

Many of these converters incorporate in the central core, a Chemetics patented radial flow gas/gas exchanger. Catalyst experience in these converters has been with Topsøe and BASF rings as well as with Chinese pellet catalyst.

Features Of The Chemetics' Stainless Steel Converter Design Which Have Proven To Be Very Successful Over The Last 11 Years

Internal Gas/Gas Exchanger

This patented feature of the converter, eliminated the hot gas duct from Bed #1 which traditionally was a serious maintenance problem with external hot exchanger designs. Initial concerns of clients, with this internal exchanger concept, were around access for maintenance. These concerns have now proven to be groundless for two reasons:

a) *No maintenance has been reported to be necessary on any of the installed units.*

b) *The converter design has been developed to allow full access to top and bottom tube shells of the exchanger, therefore providing the same access as would be possible for an external hot exchanger. Also, if necessary, the hot exchanger could be lifted from the converter core as a separate unit.*

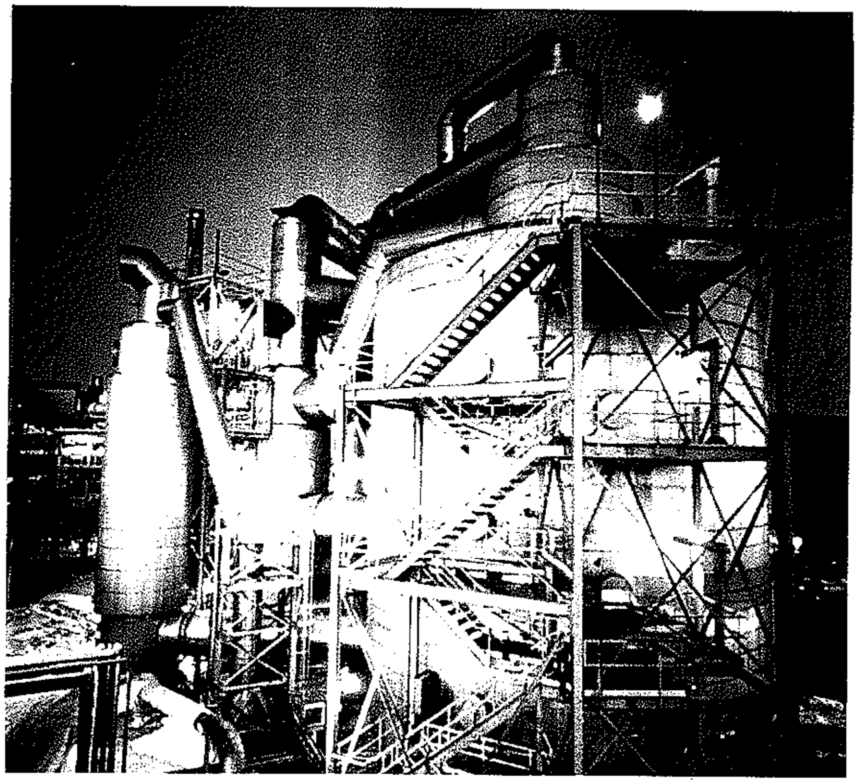


Photo No. 1

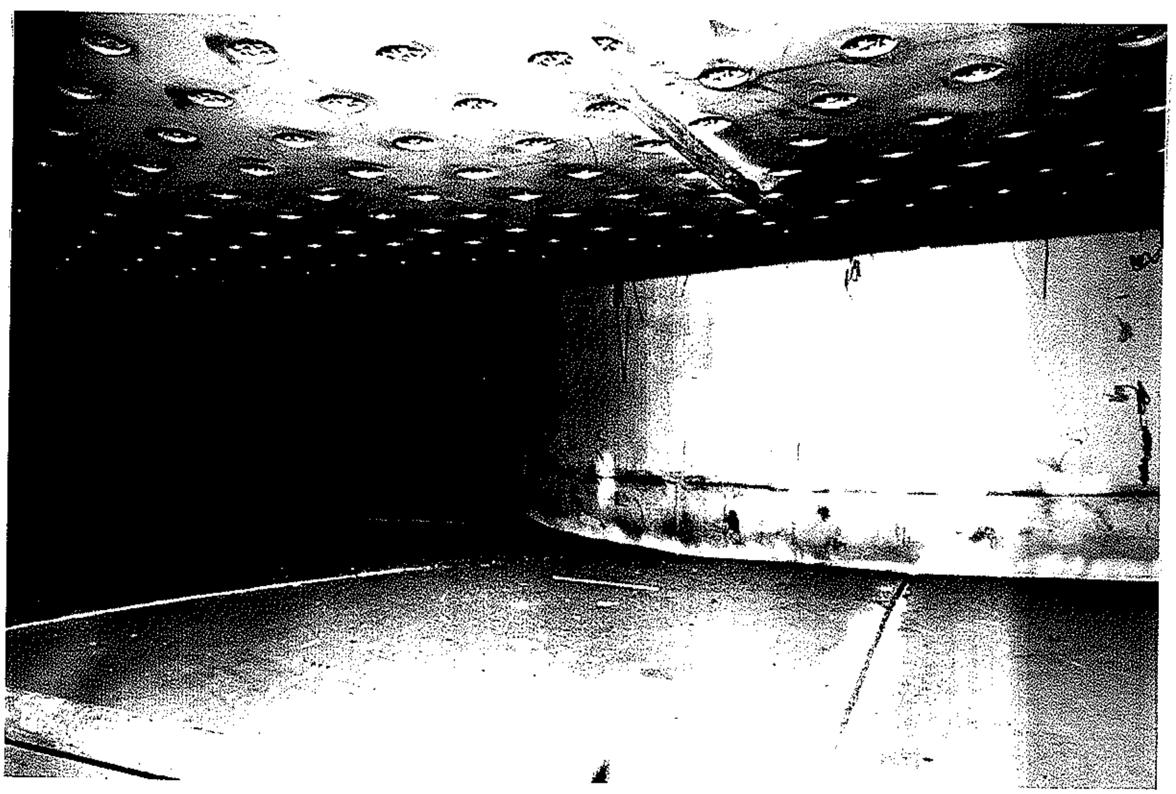


Photo No. 2

All Welded Construction

This feature has eliminated the gas bypassing problems associated with conventional cast iron grid and post designs. Operators and catalyst screening companies have learned to fully appreciate the open access the design provides above and below each bed. See photograph No. 2.

High Temperature Strength of Stainless Steel

Removal of the requirement for refractory brick lining and metallizing has eliminated these high maintenance areas common with conventional converters. Positioning of Bed #1 at the base of the converter, made possible by the use of stainless steel, has also proven to considerably ease catalyst screening procedures.

Rapid Heat Up Time

The unique Chemetics "BLOOPER" design of catalyst bed support has proven to prevent thermal stress problems associated with competitive flat plate designs, thus allowing rapid plant startup times with no restriction on temperature differentials between beds. The low heat capacity of the stainless converter also assists with rapid startup. Client concerns of a corresponding rapid cool down have proven unjustified because rate of cool down is associated with insulation efficiency and internal flow control.

Circular Ducts

Replacement of "mouth organ" type nozzle designs with circular nozzles has eliminated maintenance problems previously experienced with converter nozzle connections.

Radial Flow Gas Distribution

Introduction of gas to each bed via radial flow from the converter core or via multiple entry pipes, has ensured maximum utilization of the catalyst in all installations.

Converter Fabrication Methods

The all welded construction combined with the core tube design, has enabled Chemetics' converter to be fabricated by a variety of methods, each one customized to site and client requirements. The main three methods employed in converter fabrication/erection have been as follows:

Fabrication Method (1)

Large diameter converters have usually been built from piece plate parts as is common practice with storage tanks. The multiple annular beds construction and thin plate design has proven to require a high level of expertise in plate fit up and welding. Over the years, Chemetics has established simple and effective procedures which ensure concentric construction of shell and core as well as uniform dishing of bed support plates for this method of manufacture. Comprehensive welding plans and quality control procedures have also been developed to ensure clients receive a high integrity vessel. See photograph No. 3.

Photo No. 3

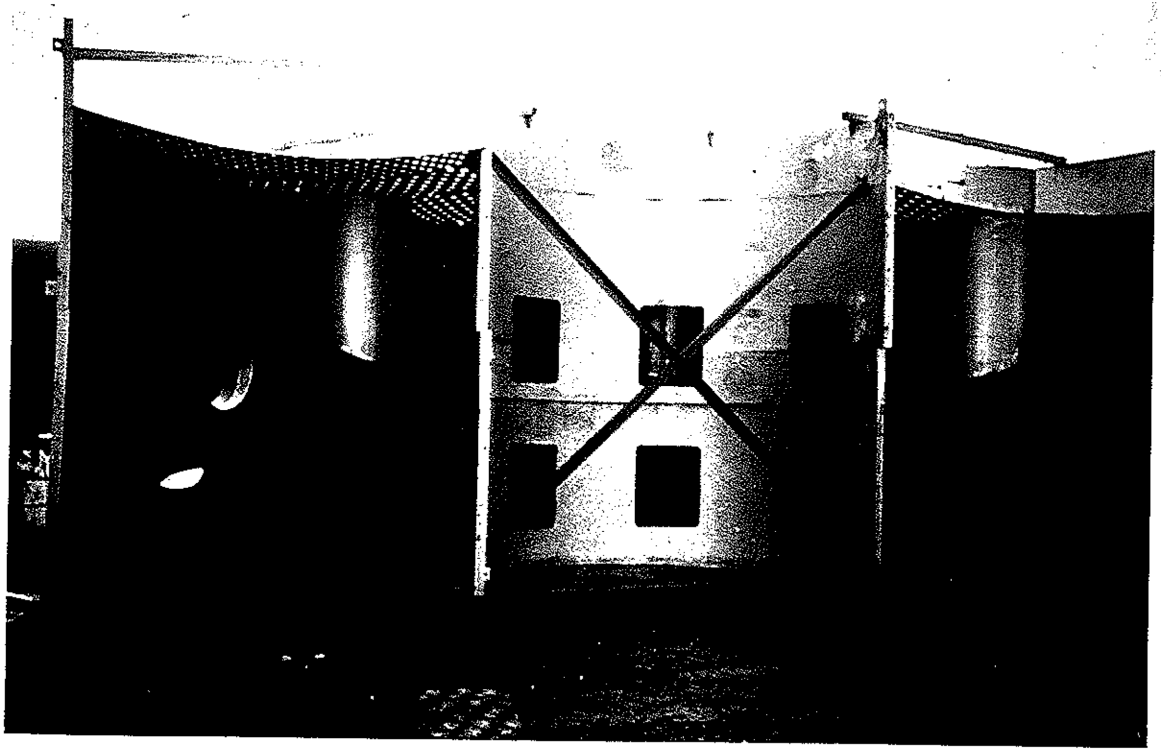


Photo No. 4

Fabrication Method (2)

Medium sized converters have been partially shop fabricated in multiple levels of 180° or 120° sections. These sections shipped complete, considerably simplify field fit up and final welding. High weld quality and dimensional accuracy can be maintained by this preferred method of construction. See photograph No. 4.

Fabrication Method (3)

Small diameter converters have been shop fabricated complete or in multiple 360° sections. The highest weld quality and dimensional tolerance can be ensured by this manufacturing method. See photograph No. 5.

Converter Installation

Independent of fabrication technique employed the light welded stainless steel design of Chemetics converter facilitates single lifts and transfer by crane of completed units from temporary, to permanent foundations. This significant feature considerably reduces plant turnaround time when converters have to be replaced. The simple lift concept is feasible for units as large in diameter as 42 ft.

Plant Design Advantages

The core design of the Chemetics converter enables plant layout to be simplified by the insertion of one or two gas exchangers or alternatively a combination of superheater and gas exchanger. This patented feature of Chemetics converter has considerably simplified ducting complexity and eliminated the corresponding associated maintenance problems. See Illustration No. 6.

Developments of Chemetics Converters

New design currently being evaluated are:

a) *Six bed units to handle strong SO_2 strengths.*
b) *Isothermal concepts.*
c) *Pressure vessel code compliant units for higher pressure applications and for units installed in countries that impose national pressure vessel codes on new converters.*

Converter "Flaking"

Carbon steel converters exhibit severe scaling or flaking especially in the higher temperature beds. This problem has been minimized by brick lining and/or metallizing. Despite these precautions, conventional converters suffer catalyst contamination by “flaking” debris.

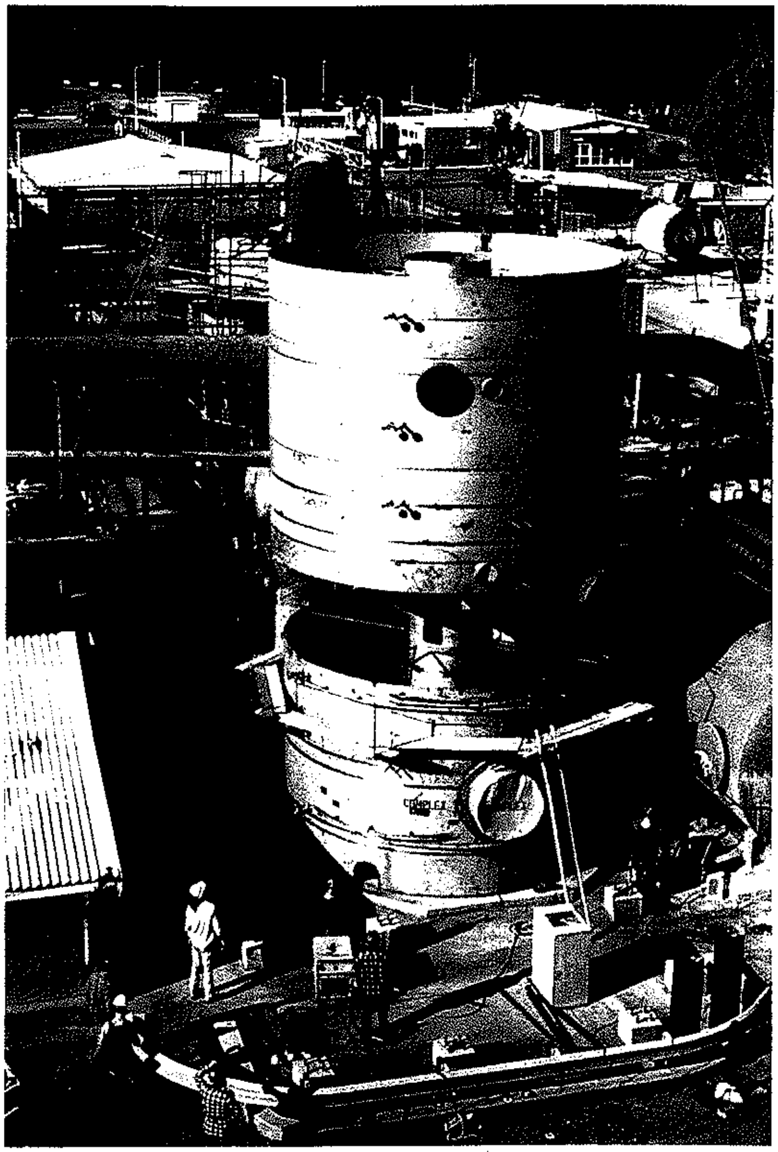


Photo No. 5

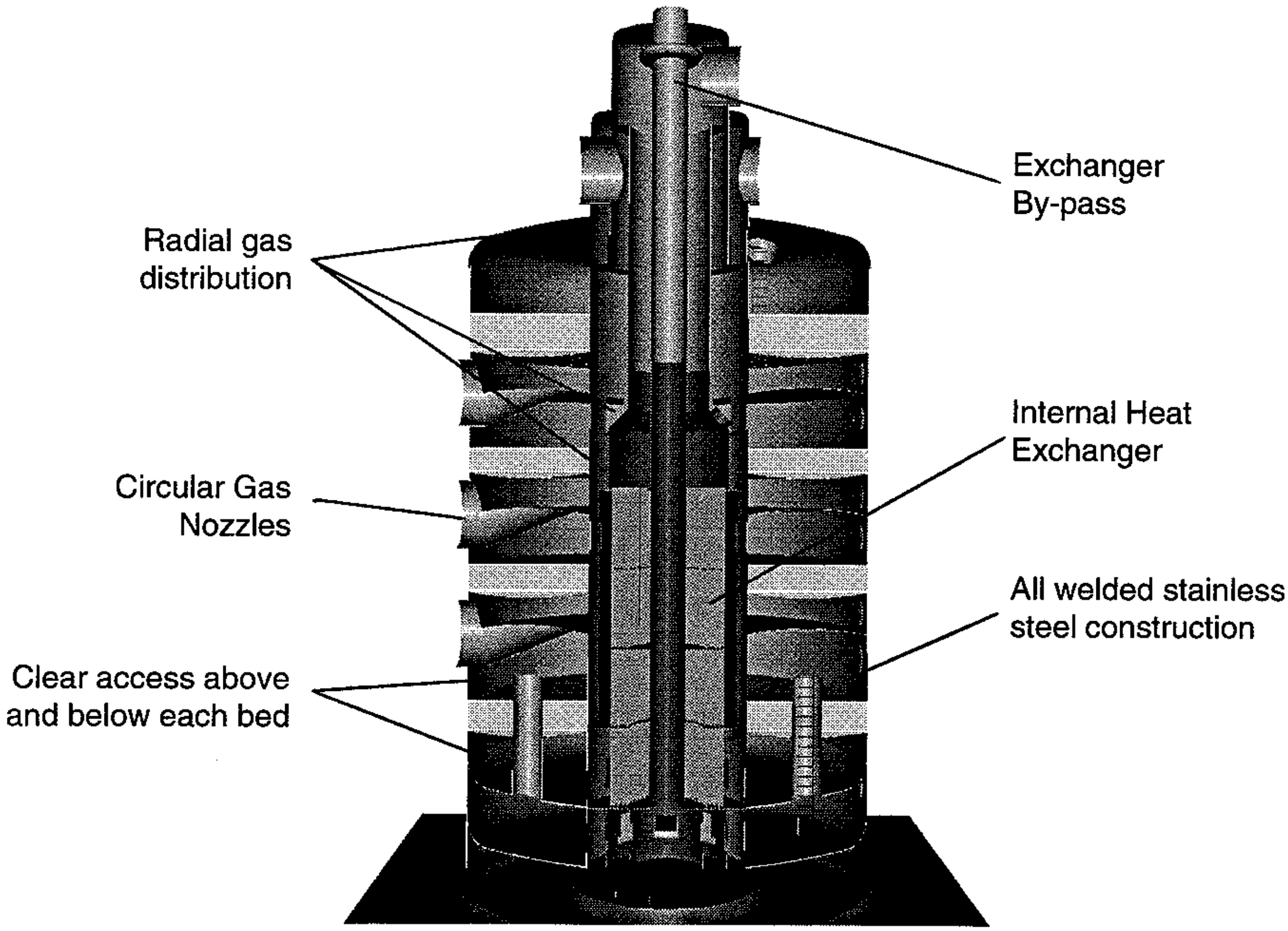


Illustration No. 6

With the advent of stainless steel converters, it was confidently predicted that scaling or "flaking" problems associated with carbon steel converters, would be eliminated. This expectation has generally been proven correct except in certain isolated applications in metallurgical acid plants. Two converters are known to the writer to have been reported as a having excessive "flaking". One is a Chemetics installation and the other is a stainless converter installed by another acid plant contractor. Both units are on metallurgical acid plants.

No problems have been seen or reported with stainless converters installed on sulphur burning or regeneration acid plants and no problems have been seen or reported to date on other stainless converters in metallurgical acid plants. Chemetics experience with stainless converters on metallurgical acid plants dates back to 1983. One 4 bed unit which has been in continuous operation since 1985 on a metallurgical acid plant, has been regularly inspected and never seen to experience a flaking or scaling problem.

The internal surfaces of 304H converters typically develop a dark grey surface discolouration within a few months of operation. With time, the discolouration thickens into a thin black scale which may be mottled with rust or whitish coloured compounds (Figs. 1, 2, 3). Mature scale thicknesses are normally in the 0.05 - 0.1 mm range and the scale material is hard and brittle. These statements describe the general experience in Chemetics designed converters, but the amounts and characteristics of the scale can vary somewhat from plant to plant depending on process parameters.

The surface darkening and scale formation occurs by high temperature gas/metal chemical reactions, involving oxidation and sulphidation of the steel's constituent elements. These reactions are governed by chemical thermodynamics and reaction kinetics and are influenced by gas composition and temperature. Gases with high Sulphur content, low Oxygen content and high temperatures are believed to be the most aggressive to stainless steel and result in the greatest scale forming potential.

The corrosion resistance of 304H stainless steel to the SO_2, SO_3, O_2 and high temperature converter environments stems largely from its nominal 18% Chromium content. The Chromium in the alloy reacts with the oxidizing gas to form a stable, dense, and adherent Chromium oxide (major component) and sulphide (minor component) layer which protects the underlying metal from further reaction. The layer acts as a barrier to the diffusion of metal atoms outwards and to the diffusion of Oxygen and Sulphur inwards. As long as a compact Chromium oxide/sulphide layer forms and remains undamaged, further scale formation can only occur at a very slow rate.

In order to form the required Chromium oxide/sulphide protective layer, the metal surface must become enriched in Chromium until its concentration becomes sufficient for the element to be preferentially reacted. At the elevated converter temperatures, the stainless steel does this through bulk material to surface diffusion of Chromium and removal of the other stainless steel matrix elements, predominantly iron, through reactions with the O_2, SO_2, and SO_3 process gases. When 304H stainless steel is exposed to the oxidizing converter gases, its Iron and to some extent its Nickel components react more rapidly with the atmosphere than does the more stable Chromium. They diffuse outward relatively rapidly to react closer to the

Figure1
Typical Appearance of Bed No. 1 Outlet

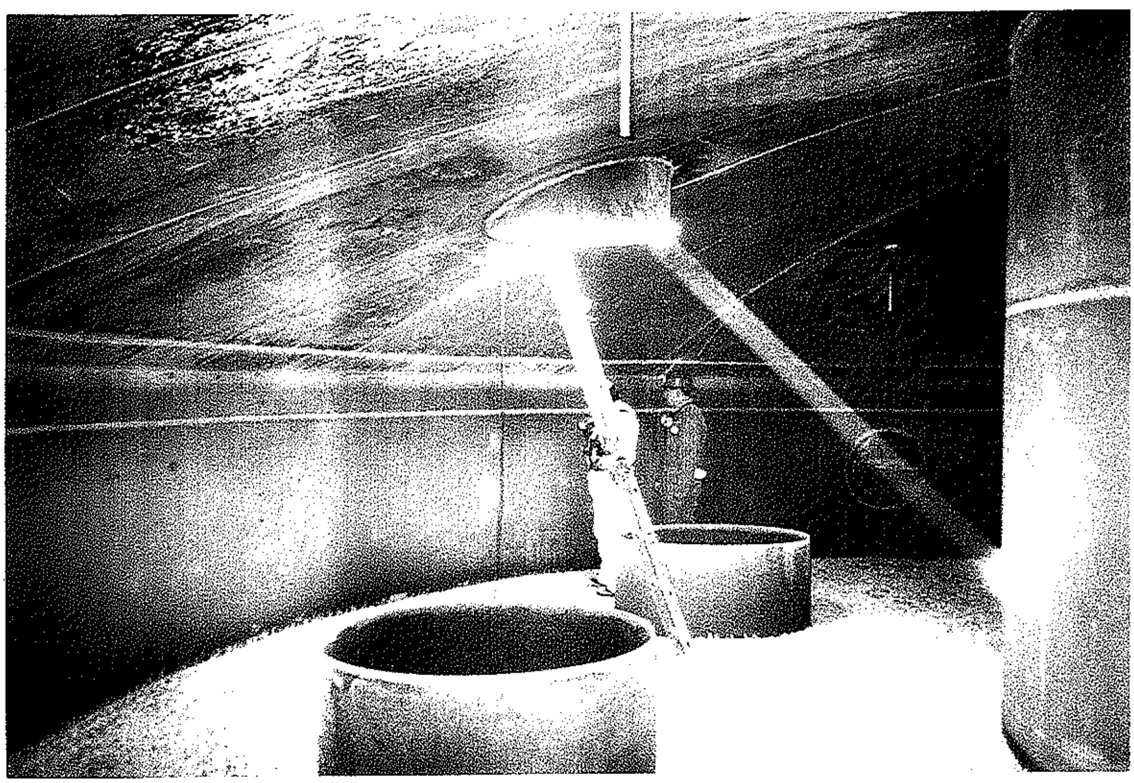


Figure2
Typical Appearance of Bed No. 1 Inlet

Figure3
Typical Appearance of Bed No. 1 Outlet Area Converter Core

scale/gas interface. The result is a duplex surface scale on the stainless steel, consisting of a black outer layer of Iron oxide and metastable Iron sulphide and an inner protective one high in Chromium.

It is the outer black layer of Iron oxide and sulphide which is the converter scale "flake" seen during annual vessel inspections.

Fig. 4 provides a representation of the oxide/sulphide layers which form on stainless steel converter surfaces during long term exposure. The sketch and above description are an oversimplified view of the process, as complex oxysulphides are present throughout the surface layer and definite transition regions exist in its structure, but they provide a basic framework for discussion.

Figs. 5 and 6 are scanning electron microscope images showing the surface morphology of a stainless steel sample taken from the wall of an actual converter after approximately five years in service. The metal sample was taken from the hottest region of the converter (Bed #1 outlet) and the micrographs represent the area of heaviest scale formation on the piece. The lamellar structure at the metal to oxide/sulphide interface is the protective Chromium rich layer, while the thicker, solid appearing upper scale is the Iron oxide/sulphide. The lamellar Chromium oxide structure gets finer and more coherent as the metal surface is approached.

Figs. 7 and 8 are scanning electron microscope energy dispersive X-ray (SEM EDX) elemental analysis data reports from regions A and B in Fig. 6. The data is only considered qualitative, but with the exception of Oxygen, the peak heights reflect the relative amounts of the elements present. Small Oxygen peaks on these graphs still indicate significant quantities of the element. The results show that the outer scale consists mainly of Iron, Oxygen and Sulphur and these are believed to be combined in a mixed layer of Iron oxides and sulphides. The inner layer analysis shown in Fig. 8 indicates a Chromium, Oxygen, Sulphur, Iron composition which is believed to present as Chromium oxide (major constituent), Chromium sulphide, Iron oxide, Iron sulphide and mixed Chromium and Iron oxysulphides.

Additional analytical work has been performed on black scale "flakes" found detached from the converter walls inside the vessels. The same analysis has been performed on scale particles taken from two converters, with similar results. Figs. 9 and 10 give SEM EDX elemental analyses for both the process gas exposed surface and the protected internal surface of a typical scale flake. The data shows that the flakes are composed of a mixture of predominantly Iron, Sulphur and Oxygen, which are believed to be present as Iron oxides and sulphides within the flakes. Also present in the flakes are small quantities of Nickel, probably as sulphide and gas stream impurities. The figures show a difference in chemistry between the gas exposed front side and the protected back side of the flakes. The front sides have a larger Iron oxide content than Iron sulphide content, while the reverse is true for the back side of the flakes. The composition of the detached scale varies with thickness because of the concentration gradients of the various scale forming compounds which exist in it during formation. Thermodynamics, reaction rates and the effective concentrations of the reactants dictate the types and amounts of compounds formed. Significant quantities of Chromium are not normally detected in the scale flakes, indicating that the protective Chromium rich layer is not greatly affected by flake formation.

Figure 4
Simplified Representation of the Surface Layers Formed on the Inside of Stainless Steel Converters

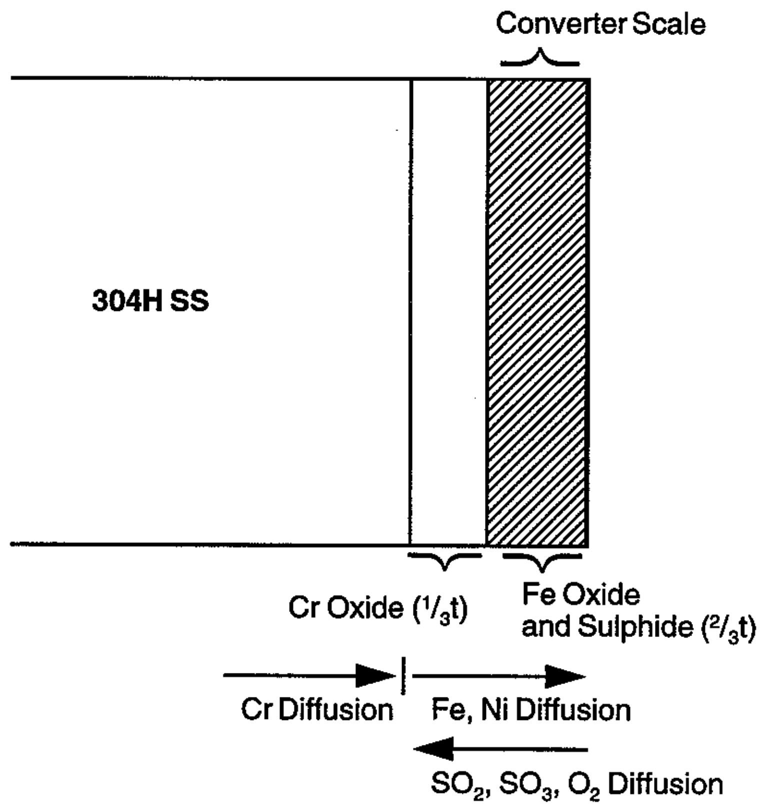


Figure 5
SEM Image of
Stainless Steel Converter
Surface structure

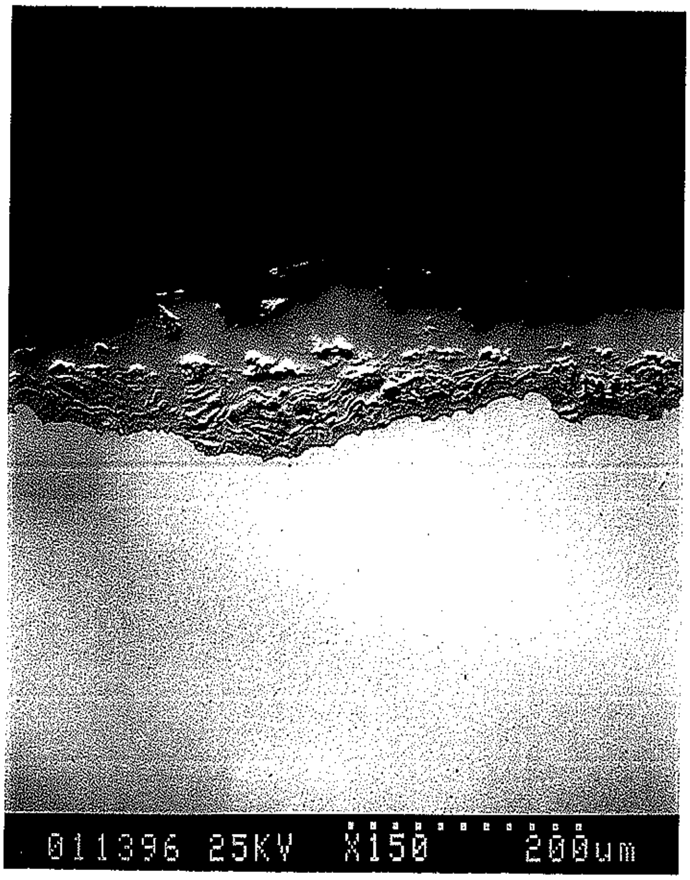
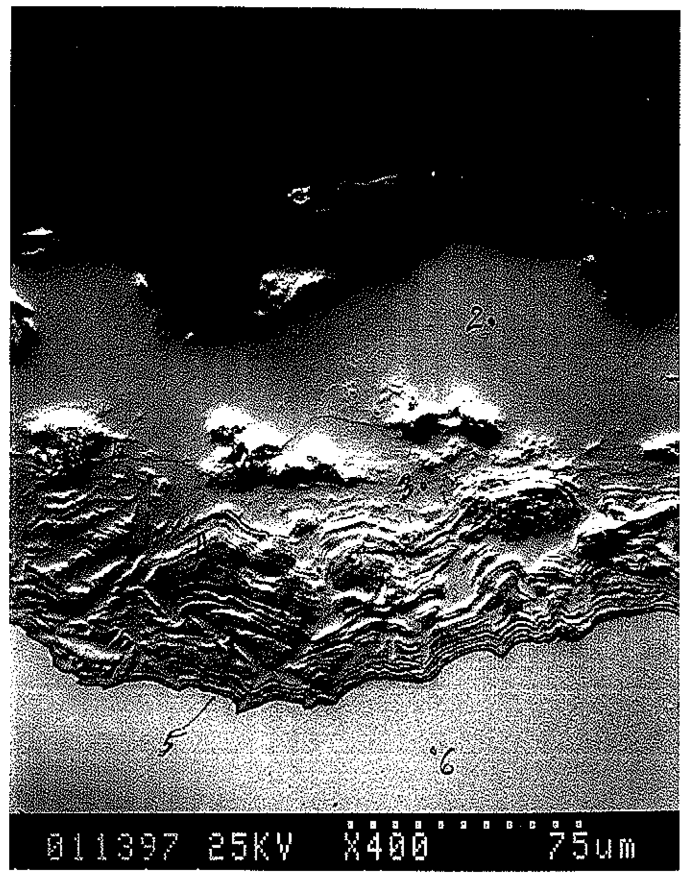


Figure 6
SEM Image of
Stainless Steel Converter
Surface Structure
(higher magnification)



Acid plant converters are exposed to both complex mechanical stresses and a complex corrosive environment. The mechanical properties of the surface films formed on stainless steel converters control their long term stability and hence the equipment's metal loss rate and the amount of scale formed. Oxide and sulphide scales have low ductility, but sulphide scales are generally considered more fragile. Iron sulphide is brittle and contains numerous internal defects, while the dense protective Chromium oxide layers formed on stainless steel possess a limited amount of ductility and resistance to deformation. Strains imposed on the oxide/sulphide surface through thermal movements, mechanical movements, creep, oxide/sulphide layer growth and repair processes, etc. cause cracking damage in the surface films and may lead to scale spallation. Gas velocity can also be a factor in the scale damage and removal process, as higher gas velocities tend to lift cracked scales, spreading damage and creating particulate. Gas flow and turbulence can entrain scale particles and deposit them in locations away from their points of origin.

The formation of the loose black scále flakes described and reported earlier, is rationalized by the separation of the Iron oxide/sulphide upper scale from the lower Chromium oxide layer. Figs. 9 and 10 indicate that brittle Iron sulphide tends to concentrate along the bottom fracture surface of the flakes. The presence of Iron sulphide facilitates cracking separation and flake formation. The majority of the scale cracks and flakes are believed to be created when the vessel experiences the large thermal movements associated with a shutdown heat-up and cool-down cycle. Once the vessel has experienced its first shutdown cycle, additional scale flakes may be separated from the vessel wall by smaller mechanical and thermal movements and gas turbulence. There is little evidence to suggest that any significant damage is done to the oxidation/sulphidation resistant Chromium oxide film during this process and the converter environment is well suited for the use of stainless steel because the oxidizing gas mixture facilitates rapid healing of minor cracks in the Chromium rich layer. The black flake material is believed to be largely the removal of the Iron oxide/sulphide layer which forms during the vessel's initial surface conditioning period, with a smaller on going contribution being made by the film's dynamic growth and repair processes.

Over the last 14 years, Chemetics has constructed about 20 304H stainless steel SO_2 converters and a large number of gas/gas exchangers built from the same alloy. Ultrasonic thickness tests have been performed on many units at various stages of their service lives and although minor black surface deposits were identified in most cases (see Figs. 1,2,3), no metal loss has ever been detected. Some of the converters had been in service for over ten years at the time of testing.

Figs. 5 and 6 indicate a maximum scale thickness of 0.15 mm on the sample of converter material after five years in service. At the same time as the stainless steel sample was extracted, thickness tests were performed on the vessel indicating no detectable material loss. Historical Chemetics experience indicates that the volume of surface oxide and sulphide formed is always much larger than the volume of parent metal consumed.

Figure 7
Elemental Analysis of Figure 6 Location A

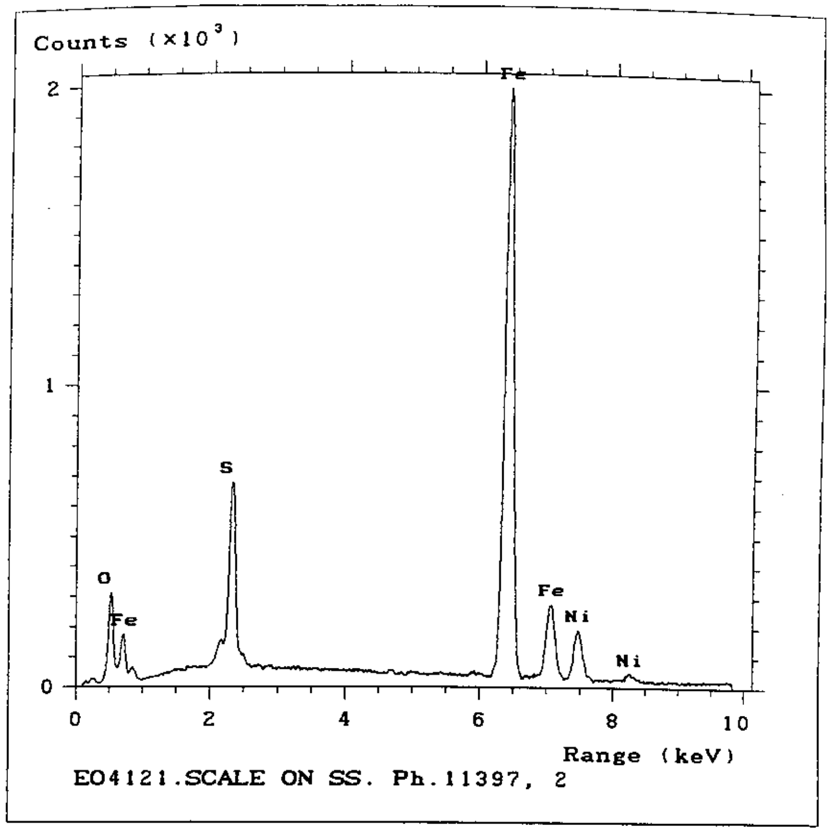


Figure 8
Elemental Analysis of Figure 6 Location B

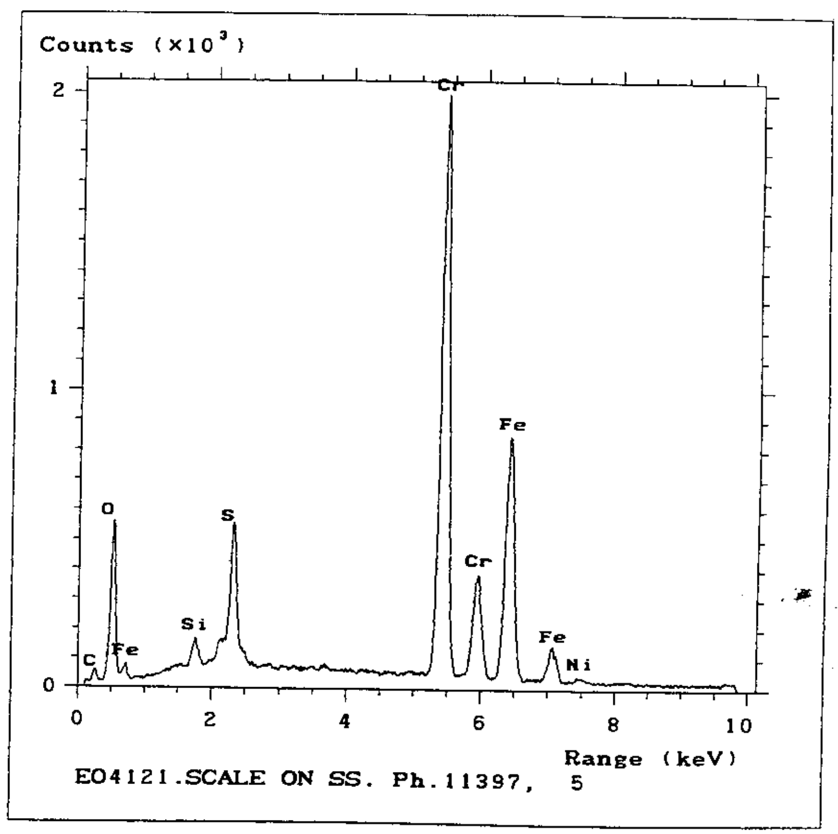


Figure 9
Process Gas Slide Analysis of Typical Scale Flake

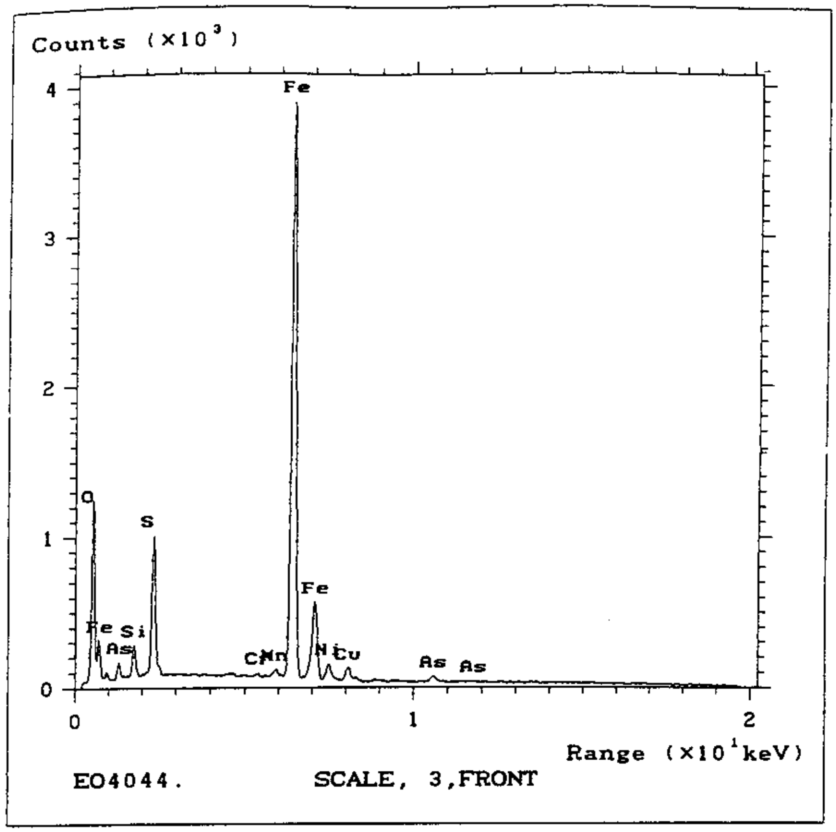
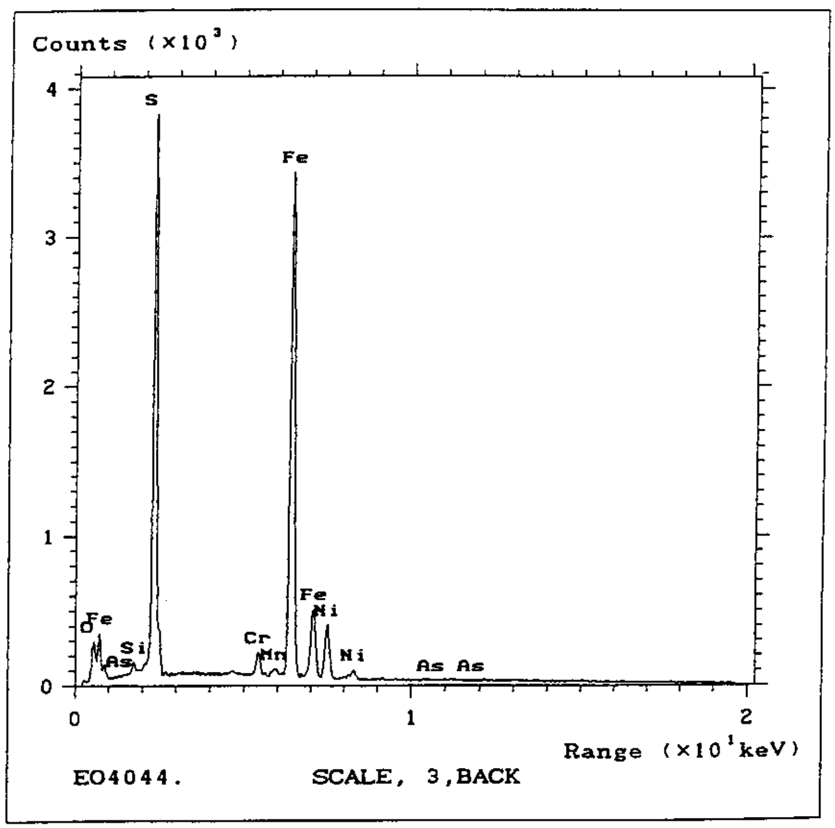


Figure 10
Metal Slide Analysis of Typical Scale Flake



Samples of 304H stainless steel have been removed from the Bed #1 outlet area of two acid plant converters for detailed analysis. In both cases the 304H material was exposed for approximately five years. The examinations indicated no detectable metal loss, internal sulphidation and/or oxidation or sigma phase formation during the high temperature exposure to the converter gases. The formation of sub-surface precipitates can significantly reduce the mechanical properties of a stainless alloy, especially its ductility. After their significant service, the converter material samples still exhibited a high level of room temperature ductility and formability.

The high temperature corrosion rates on Chemetics stainless steel SO_2 converters are extremely low and while the black Iron oxide/sulphide surface layer forms in almost all cases, it has only ever been reported as a problem once. In this instance, the client had gone five years without a catalyst bed screening and the black scale flakes were causing open area blockage and high converter Bed #1 and #2 pressure drop. this particular plant is subjected to daily thermal cycling because of the smelter mode of operation. If scale flakes are to be removed from a converter vessel during a catalyst screening or vessel inspection, care should be taken to remove only the loose flakes by vacuuming or sweeping with a soft bristled broom. This is recommended to avoid seriously damaging the protective Chromium oxide lower scale layer, which could result in the repetition of the initial surface conditioning process and the formation of significant new quantities of scale.

Stainless converters will continue to be monitored as their operating life progresses into the second 14 year period. It is confidently predicted that the original stainless units will still be operating at the end of this period and still without the maintenance problems associated with the old carbon steel/cast iron installation.