

## NOVEL SURFACE TREATMENT TO MITIGATE FOULING IN HEAT EXCHANGERS AND PROCESS EQUIPMENT

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### ABSTRACT

The global impact of climate changes due to Greenhouse Gas (GHG) emissions cannot be overemphasized. To combat this, engineers are constantly striving to develop innovative enhancements for heat transfer and fouling reduction in process equipment as a pathway to reduce CO<sub>2</sub> emissions. A novel surface application of Minimox® treatment, a water-based suspension of rare-earth oxides, is a promising solution. The self-protective alloy treatment, unlike a traditional continuous coating, has no measurable thickness, does not impose any operating temperature limits, protects from high temperature oxidation, and decreases surface energy and polarity that leads to low fouling and coking rates. Minimox can be applied by dipping or spraying to both external and internal surfaces, including non-conventional tubing shapes. A post-application curing at 400°C for 1 hour is needed to ensure maximum fouling mitigation efficacy. Laboratory tests conducted to simulate operating conditions in a Coker furnace show that the Minimox-treated tubes reduce coke formation by about 80% as compared to untreated tubes. In addition, adhesion of coke to the Minimox treated tubes was significantly lower than for the untreated tubes. Field data collected in refinery applications involving Coker furnace tubes and a vacuum column wash bed are promising and lend support the laboratory results.

### INTRODUCTION

#### Metallurgy of Rare Earth Additions to Alloys for Oxidation Reduction

A novel, patented [1] surface treatment, Minimox® Self-Protective Alloy Treatment, has been developed which involves the application of a water-based suspension of rare-earth oxides. The product was developed to reduce oxidation of stainless steel-based alloys at high temperature. Details are available at [www.minimox.com](http://www.minimox.com).

Alloys designed for high-temperature applications contain certain additions, generally classed as reactive element effect (REE) materials. These additions include aluminum, silicon, scandium, titanium, yttrium, zirconium, niobium, lanthanum, hafnium, tantalum and many of the rare-earth elements. When these elements are added to a

variety of alloys, the rare earths diffuse to the material surface when heated and scale spallation is ultimately reduced in high temperature service.

Generally, the reactive element is incorporated into the alloy, but the reactive elements can also be deposited on the metal surface by various methods, including ion implantation and laser surface alloying. These methods are relatively expensive and/or cannot be applied in the field or inside complex geometries.

#### Development of Minimox® Self Protective Alloy Treatment.

In contrast, the Minimox® technology is predicated on the fact that if REE addition elements are instead applied as a low density (i.e. significantly less than a monolayer), superficial, non-continuous coating to the surface of a more basic alloy, the same high-temperature surface oxidation properties can be achieved as alloys with REE additions to the bulk. Alloy types that contain rare-earth materials as bulk additions for oxidation resistance are good candidates for Minimox-treated surfaces. These include stainless steels, magnesium and aluminum alloys, and titanium.

Minimox research has been conducted on a range of several types of REE species. Most typically, Minimox solutions based upon Y<sub>2</sub>O<sub>3</sub> exhibit superior results. The specific product grade is Minimox 721.

#### Oxidation Reduction with Rare Earth Coatings

As an example, Figure 1 shows a coupon of 410 stainless steel that was partially coated with Minimox 721 before heat treating (1010°C, 30 minutes, 760°C temper) in air. These temperatures are typically used to heat treat this alloy. The treated portion has a thin, gold-colored oxide (composed of CrMnO<sub>x</sub> and CrO<sub>x</sub>) while the untreated portion has a flaking brown oxide (chiefly Fe<sub>2</sub>O<sub>3</sub>).



Fig. 1. 410 stainless steel sample, right side treated with Minimox 721 before heat treating. The heat treatment was 1010°C for 30 minutes followed by a 760°C temper, all in air.

Figure 2 shows the same sample as in Figure 1 in cross section, with significant metallic loss ( $\Delta 74$   $\mu\text{m}$  of thickness) due to oxidation on the untreated side.

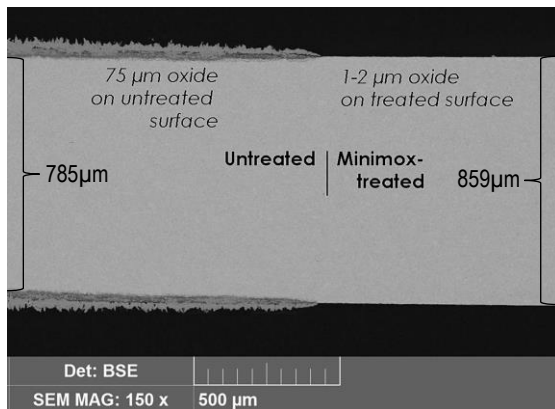


Fig 2. Cross section through coupon partially treated with Minimox Self-Protective Alloy Treatment. The Minimox-treated portion had a 1-2  $\mu\text{m}$  oxide while the untreated surface had a 75  $\mu\text{m}$  oxide. There was 74  $\mu\text{m}$  of metal coupon thickness lost to oxidation on the untreated portion.

Generally, oxidation occurs with outward diffusion – i.e. the metallic species diffuse to the surface and the oxide grows on the surface. As with alloys that contain rare earth species to minimize oxidation at high temperatures, the rare earth stays on the surface of the material because the direction of oxidation has been reversed. Oxygen must diffuse through the layer to react with the metal. The small grain size of nanooxides reduces the ability for oxygen, and other species, including carbon, to diffuse through the surface towards the bulk and oxide layer grown is severely restricted.

### Carburization and Metal Dusting Reduction with Rare Earth Coatings

Figure 3 shows a 316L coupon partially coated with Minimox Alloy Treatment held in a carburizing furnace for 168 days; the atmosphere was endo gas approximately (20% carbon monoxide, 40% hydrogen and 40% nitrogen, trace amounts of carbon dioxide) at 760°C (1400°F). Minimox treatment protected the alloy in this environment.



Fig. 3. 316L coupon partially treated with Minimox, held in a carburizing furnace for 168 days at 760°C.

Figures 4-5 compare untreated and treated coupons of Alloy 601 after metal dusting testing at Argonne National Laboratory at 600°C for 4286 hrs. The Minimox-treated coupon was preoxidized before testing. Pitting, present on the untreated alloy, was substantially decreased on the Minimox-treated alloy.

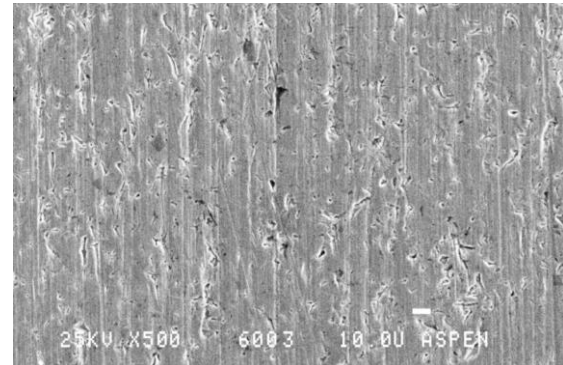


Fig. 4. Untreated Alloy 601 exposed to a metal dusting atmosphere for 4286 hours.

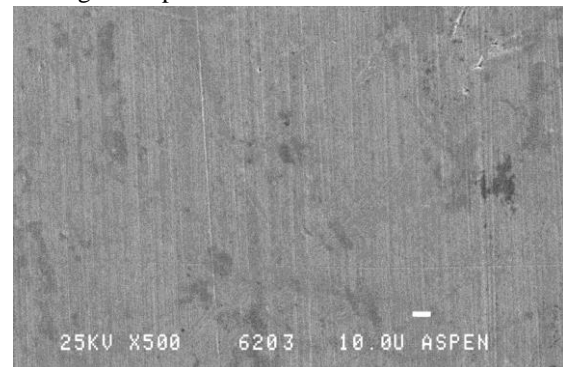


Fig. 5. Minimox-treated Alloy 601 exposed to a metal dusting atmosphere for 4286 hours

Alloys cured (400°C, 1 hr) after Minimox Alloy Treatment were tested by Chevron to determine if they provided any antifouling properties. When initial results in a laboratory fouling rig were considered promising, additional research was conducted.

## METHODS

### Fouling Reduction with Rare Earth Coatings based on Decreased Surface Energy

When it was determined that Minimox-treated surfaces were hydrophobic; this property of the surface was optimized for additional antifouling testing.

Water-based solutions consisting of suspended  $\text{Y}_2\text{O}_3$  nanoparticles ( $\approx 5$  nm) and a surfactant were applied to a variety of alloys via dipping methods. The alloys included stainless steels, superalloys, titanium, 1008 carbon steel, and T5 and T9. One side of most coupons contained the mill oxide; the other side was ground to a 200 grit metallic finish. After solvent cleaning and coating, each of the alloys was heated in air at selected temperatures (400°C-

700°C). Kinetic experiments were also conducted where each alloy was heated at specific temperatures for increasing periods of time.

The surface free energy (SFE) of each coupon was quantified with multi-point sessile droplet contact angle measurements, as shown in Figure 6.



Fig. 6. Sessile contact angle measurement demonstrating hydrophobicity with water on a Minimox coated coupon.

All contact angle measurements were carried out with a Krüss MSA Mobile Surface Analyzer using a droplet size of 2  $\mu\text{L}$ . The Krüss measurements were subsequently validated across droplet sizes ranging from 2 – 10  $\mu\text{L}$  with a Ramé-Hart Model 590 automated tensiometer. The general layout and configuration of the Ramé-Hart instrument is depicted in Figure 7.

To resolve the disperse and polar components of total SFE, both the Krüss and Ramé-Hart instruments used water and diiodomethane as the droplet media. Data reduction was carried out in accordance with the methods proposed by Fowkes [2] as well as Owens and Wendt [3], Rabel [4], and Kaelble [5], with the latter cluster of authors generally being collectively associated with the Owens-Wendt-Rabel-Kaelble (OWRK) model.

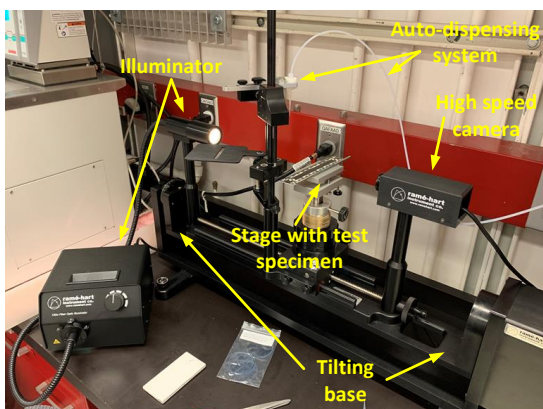


Fig 7. Ramé-Hart Model 590 automated tensiometer used for coupon SFE measurements.

Quantifying the polar component of total SFE permitted the surface polarity to be calculated as

$$\% \text{ Surface Polarity} = \frac{SFE_{polar}}{SFE_{total}} \quad (1)$$

Fouling propensity of the Minimox treated tubes was carried out using the laboratory apparatus described by Jackowski et al. [6] and Cibotti et al. [7] In essence, fluid flows upward in a vertical annular space between a heated and outer housing tube. To accelerate fouling, fluid velocities are very low resulting in wall shear stresses of nearly zero. The experiments are run at constant tube wall temperatures, i.e., heat flux is reduced if fouling occurs. The test rig allows for both once-through and recirculating modes of operation.

## RESULTS AND DISCUSSION

### Surface Energy Optimization

When samples were initially coated with Minimox Alloy Treatment and heated to defined test temperatures, the surfaces were found to be hydrophilic. It was determined that after approximately 3 days in air, the surfaces became hydrophobic. The surface energy and surface polarity as a function of time are plotted in Figure 8.

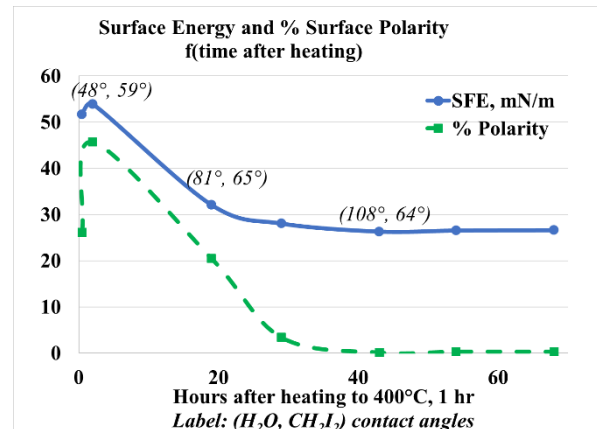


Fig 8. Surface energy and % surface polarity as a function of time after heating (400°C, 1 hr).

All surface energy data in this paper were obtained after the 3-day hold time illustrated in Figure 8.

Doing an initial on-line search, it is easy to find discussions of rare earth hydrophobicity. More extensive research has indicated the answer is not as straightforward.

Several research publications indicate rare earths (RE) are hydrophobic materials. Work done by a group at the Massachusetts Institute of Technology in 2013 by Azimi et al. [8] has stated: “In summary, we show that (rare earth oxides) REOs over the entire lanthanide series are intrinsically hydrophobic.” Hydrophobicity of  $\text{CeO}_2$  has been noted by Lv, et al. [9] and Sin-Pui, et al. [10] and for  $\text{La}_2\text{O}_3$  by Xiao, et al. [11].

Subsequent research into the cause for the time delay requirement has found there are disagreements in the literature regarding the inherent hydrophobicity of rare earth coatings. Preston et al.

[12] state “The results indicate that REOs are in fact hydrophilic when clean and become hydrophobic due to hydrocarbon adsorption...at long times (>4 days).” It was similarly noted by Wang, et al. [13] that hydrocarbon adsorption was necessary for ceria hydrophobicity.

Finally, Lundy, et al. [14] published work on hydrophobicity of sintered CeO<sub>2</sub> as well as sputtered films of HfO<sub>2</sub> and ZrO<sub>2</sub> and thermally grown SiO<sub>2</sub>. He confirmed the adsorbed hydrocarbon theory by exposing the surfaces to nonane vapor. After nonane exposure, the surface energy decreased from 66-72 mN/m to 10-17 mN/m.

Similar experiments were conducted at Material Interface, using heptane rather than nonane. The hydrocarbon adsorption experiments did not result in decreased surface energy.

To determine the changes in the surface chemistry of the treated material as a function of time, both x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) were employed. These techniques were conducted 17, 41, and 65 hours.

The XPS results are summarized in Table 1. The only species that increased consistently over the three days was iron. This implies species are being desorbed during the first three days.

Table 1. Concentration of three surfaces as obtained with XPS. Data are normalized atomic percent of elements above atomic number 3 within 5 nm of the surface.

Time after Treatment, hrs	SFE, mN/m	C	O	Fe	Y
17	34	32.6	49.6	6.6	11.2
41	27	19.9	60.2	8.3	11.6
65	26	20.2	59.1	9.1	11.6

TOF-SIMS was conducted on parallel samples. TOF-SIMS is not considered quantitative, but to compare peak intensities, the intensity ratio of key ionic species to iron at m/z = +56 was calculated. Using this method, essentially no species adsorbed during the initial three-day time period. There was no sign of hydrocarbon adsorption being required for hydrophobicity. Instead, several species desorbed. The most notable decreases occurred for the Y<sub>2</sub>O<sub>3</sub> stabilizing ion, and organo-yttria and water-yttria complexes.

Based upon our results, the Minimox-treated, yttria-coated surface is hydrophobic, without any requirement of hydrocarbon adsorption.

### Surface Energy and Fouling Propensity of Alloys

**Surface energy of alloys.** Surface energy can be defined as the excess energy at the surface of a material compared to the bulk. If this excess energy did not exist, solids would spontaneously sublime. When a solid is cut, bonds are broken and two

surfaces are generated – in this context, surface energy can be understood as being the work required to cut a bulk sample and create a surface.

Intrinsically, surface energy is related to a material’s work function. The work function is the minimum energy needed to remove an electron from a solid to a point outside the solid surface.

An extensive study of work function vs. surface energy was conducted by Skriver and Rosengaard. [15] They found “excellent agreement” between surface energy and work function for 40 elemental materials.

Transition metal oxides can have a broad range of work functions. Chemical reactions alter transition-metal oxide work functions, making their work functions difficult to control. Oxides tend to have higher work functions than their metals (but not always). Typical examples are included in Table 2.

Table 2. Work function of selected metals and oxides. [16], [17]

Metals	Work function, eV	Oxides	Work function, eV
Al	4.06 - 4.26	Al <sub>2</sub> O <sub>3</sub>	4.70
Cu	4.53 - 5.10	CuO	4.7-5.5
		Cu <sub>2</sub> O	5.0
Fe	4.67- 4.81	FeO	3.85
Mo	4.36 - 4.95	MoO <sub>3</sub>	4.25
Ni	5.04 - 5.35	NiO	5.3
Si	4.60 - 4.85	SiO <sub>2</sub>	5.00
Ti	4.33	TiO <sub>2</sub>	6.21
Zr	4.05	ZrO <sub>2</sub>	5.80
Y	3.1	Y <sub>2</sub> O <sub>3</sub>	2.00

It is noted in Table 2 the work function of Y<sub>2</sub>O<sub>3</sub> is very low and may be responsible for the low surface energy found on Minimox-treated alloys.

**Fouling Propensity of Alloys.** Teng, et al. [18] summarized calcium carbonate fouling on double-pipe heat exchanger with different heat exchanging surfaces. For crystallization fouling, they found linear growth dependence between foulant deposition and the increase in thermal conductivity of the analyzed surface. The thermal conductivity of Y<sub>2</sub>O<sub>3</sub> is 27 W/(m·K) while for chromium, iron, cobalt, and nickel it is 84, 80, 100, and 91 W/(m·K), respectively. According to Takeda et al. [19] iron oxides also have low thermal conductivity. Therefore, Minimox processing may be beneficially reducing the thermal conductivity of surfaces to reduce fouling. Berce et al. [20] referenced studies where copper exhibited the largest amount of calcium carbonate deposits, followed by aluminum and stainless steel; silicon carbide substrates were able to mitigate scaling with a decreased fouling initiation rate.

Recent work by Toparli et al. [21] at MIT discussed the relationship between optical properties and fouling. They hypothesized “matching the full



refractive index spectrum of a coating to its surrounding fluid minimizes the adhesion of all foulants.” In a related work, Yadav et al. [22] discusses how to use refractive indices to calculate the interaction energies associated with functional group phases and calculated van der Waals forces. However, as summarized by Toparli, this method “assumes that van der Waals forces will dominate attractions between colloidal particles and surfaces.” For the fouling work conducted in this project, it has been assumed that reduction of surface polarity, with a resulting reduction in strong chemical bonds between the surface and foulant, is the preferred direction. In the surface energy measurements reported in this project, the van der Waals forces are consistent with the dispersive fraction of the total surface free energy.

**Surface Energy and % Surface Polarity and Fouling.** There were several publications that discussed decreased fouling correlated to a decrease in surface energy. A few of the papers also correlated surface polarity (defined by Equation 1) to fouling.

Azimi et al. [23] generated a series of surfaces (organosilanes) with variable surface energy and variable % polarity. The formation of  $\text{CaSO}_4$  scale was compared. There was a “significant reduction in scale formation with decreasing surface energy.” Furthermore, the polar component of the surface energy was the key factor in determining scale growth on the substrate. Samples with low % surface polarity had the lowest scale growth.

Halvey et al. [24] presented a lengthy publication on overall design of surfaces for controlling fouling in general. Overall, whatever the application, they state “Minimizing the energy of a surface reduces the strength of any potential adhesive interaction between the surface and a fouling material, known as the work of adhesion,  $W_a$ .” Controlling surface texture and roughness is also stated as being a key parameter – roughness increases contact area and the potential for mechanically interlocking surfaces, again hindering debonding. Deformation mismatch, between a surface and a foulant, can also increase the elastic strain energy of the surface system, again hindering debonding. It is stated that “minimization of the elastic modulus of a surface will have a significant, and often dominating, effect on foulant adhesion.”

Bargir et al. [25] compared calcium carbonate fouling on a variety of surfaces, including stainless steel, gold, aluminum, titanium nitride and PTFE. For relatively smooth surfaces, adhesion was influenced by the % surface polarity. For rougher samples, the topography was most likely to control deposit adhesion. Jimenez et al. [26] likewise claimed that roughness was the overriding parameter for stainless steel dairy fouling; when the roughness was less than 50 nm, hydrophobicity became the preponderant parameter.

### Surface Energy of Minimax-Treated Alloys

Various alloys were coated with Minimax and heated to selected temperatures. The surface energies of the 200 grit ground- and mill oxide-surfaces were measured, including the disperse and polar fractions. Typical data for 316 stainless steel is shown in Figures 9-10. The data in Figures 9-10 showed that for 316L, the temperature for optimum surface energy and percent surface polarity was 400 °C for one hour.

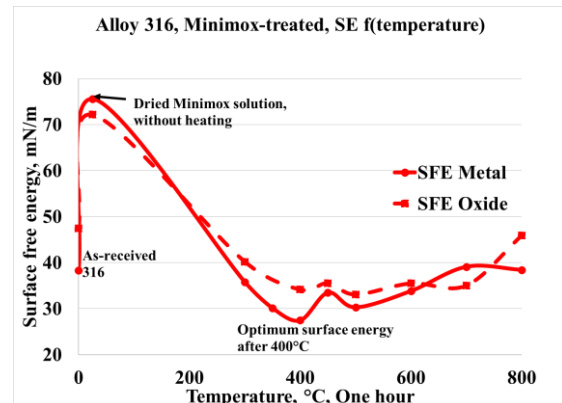


Fig. 9. Surface energy of 316L stainless after coating with Minimax 721 and heating for one hour at various temperatures

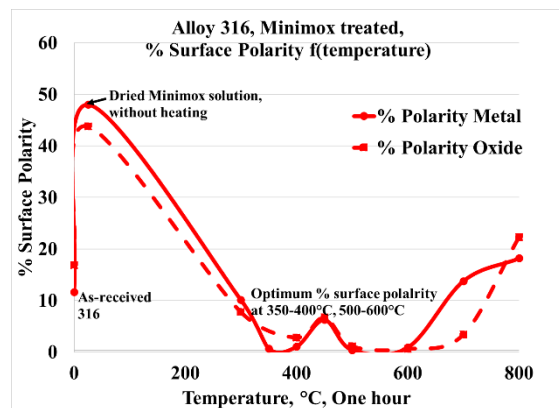


Fig. 10. Percent surface polarity of 316L after coating with Minimax 721 and heating for one hour at various temperatures.

Kinetic experiments were also conducted to determine the effect of time on the surface energy and surface polarity. Selected data are included in Figure 11. The data in Figure 11 illustrates that heating the sample for longer times at 400 °C in air still leads to very low percent surface polarity.

Similar studies were conducted on 11 alloys. Table 3 summarizes the surface energy measurements on selected alloys after rare earth treatment and heating to 400 °C for one hour in air, followed by a 3-day hold time. For each of the alloys studied, all surfaces, both metallic and oxide, became hydrophobic with Minimax treatment. All

surfaces, both metallic and oxide, had decreased surface energy with treatment. All surfaces, both metallic and oxide, have *substantially* decreased % surface polarity with treatment.

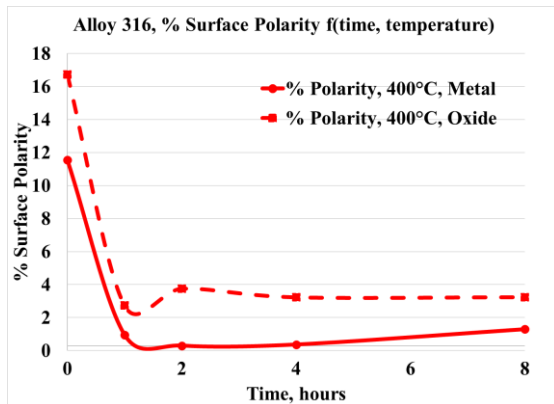


Fig. 11. % Surface polarity of 316L after coating with Minimox 721 and heating to 400°C in air for various times.

The values in Table 3 are an average of 6-12 measurements, with a standard deviation of generally less than 3%.

Table 3. Surface free energy (SFE, mN/m), and % surface polarity (%SP) of selected alloys for 200 grit Ground Surface (as-received and after treatment) and Mill Oxide Surface (as-received and after treatment).

Alloy	Property	Ground Surface As-Rcvd	Ground Surface, Treated	Mill Oxide As-Rcvd	Mill Oxide, Treated
200	SFE	35.35	26.86	41.72	29.52
	%SP	14.23	0.07	10.88	0.68
316	SFE	38.3	27.4	47.47	34.16
	%SP	11.25	0.33	16.43	2.43
317	SFE	33.90	27.01	50.15	30.03
	%SP	2.48	0.19	25.34	0.76
347	SFE	44.91	32.16	64.21	34.2
	%SP	21.69	0.31	33.09	0.06
825	SFE	36.89	23.47	55.54	28.33
	%SP	3.33	0.89	33.15	0.25
F5	SFE	52.92	23.01		
	%SP	33.00	0.17		
Ti Gr 2	SFE	37.14	29.86	49.00	32.09
	%SP	7.30	0.30	14.27	2.31
1008	SFE			50.79	33.27
	%SP			26.60	0.0

### Fouling Resistance of Minimox-Treated Alloys

Fouling resistance tests for the Minimox-treated tubes were performed with vacuum residue in the once-through mode and a test tube temperature of 538 °C which corresponds to the skin temperatures

in the Coker furnace tubes located near the exit. At ambient conditions, vacuum residue is solid, and it needs to be melted at a temperature of nearly 200°C to allow for flow in small tubing. The challenge is that too low temperatures cause solidification, leading to plugging, and too high temperatures cause coking, leading to plugging as well. The once-through operation limited the test run to 16 hours. The experimental results shown in Figure 12 indicate significant improvement for the Minimox-treated test tube.

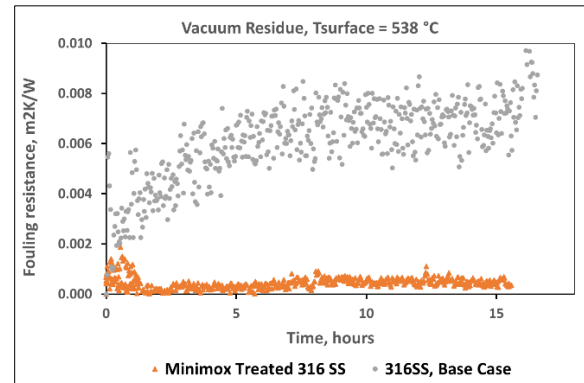


Fig. 12. Fouling resistance for untreated (Base Case) 316 SS and Minimox treated 316 SS test tube in a once-through experiment.

As highlighted in Figure 13, examination of the test tubes after the experiment revealed that the Minimox treatment reduced coke formation by about 80% and adhesion of coke to the test tube was found to be greatly reduced as well.

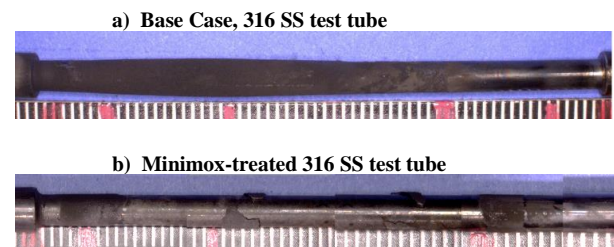


Fig. 13. Test tubes after fouling resistance experiment for vacuum residue (see Figure 12), a) untreated 316 SS tube (base case), b) Minimox-treated 316 SS tube.

Similar fouling resistance tests were carried out for lighter, less challenging process fluids handled in the refineries. These experiments were performed in a recirculation mode for 40-50 hours with 316 SS tubes. The results led to similar conclusions that the Minimox treatment of stainless steel tubes reduced fouling rates and the accumulation of deposit.

Unfortunately, performing enough interrelated fouling resistance experiments to validate the postulate that surface energy and polarity play a key role in the reduction of fouling rates was not possible at this juncture. Additional validation of this hypothesis is further complicated by the fact that

surface energy and polarity measurements are quite challenging for small tubes and that measuring the surface characteristics after a given experiment requires any fouling deposits to be removed, which introduces additional uncertainty.

### Industrial Applications of Minimox Treatment in Petroleum Processing

The laboratory scale experiments for Minimox-treated coupons and tubes indicated strong potential of reduction in fouling and coking rates in actual process equipment. To scale up the procedures applied in a pristine laboratory environment to industrial processes, Chevron initiated a collaborative effort with Material Intertec Inc. (the technology developer) and Curran International (the technology applicator). This study resulted in development of specific shop procedures, including quality assurance, for various type of process equipment.

The first technology deployment in the Oil and Gas Industry was for a crude unit vacuum column wash bed (316 SS), as shown in Figure 14.



Fig. 14. Crude Unit Vacuum Column wash bed (316 SS) installed in July 2020.

At the time of this publication, this Minimox-treated wash bed has been in continuous operation for nearly two years without showing any pressure drop buildup due to coking.

The second industrial deployment was carried out for a tube replacement in a Coker furnace (see Figure 15). In this case, one of the 20 m long, 4-inch diameter, 347H SS furnace tubes had to be replaced due to bending. Infrared temperature measurements performed after about 5 months of operation indicate lower coking rates in the Minimox-treated tube than in the adjacent non-treated tubes.

As mentioned before, the Minimox technology can be applied to complex geometries such as

enhanced heat transfer surfaces. Figure 16 shows a tube bundle with low density (630 fins/m) low fin tubes. The Minimox treatment was applied to both the outside and inside tube surfaces in this exchanger bundle. This exchanger will be installed in the summer of 2022 with expectations of significant improvement in thermal efficiency and reduction in fouling rates. If successful, this installation will not only contribute to reduction in CO<sub>2</sub> emissions but also improve plant integrity as previously described by Jackowski et al. [27]



Fig. 15. Coker furnace pipe replaced with Minimox-treated pipe, upper pipe (347H SS) installed in October 2021.

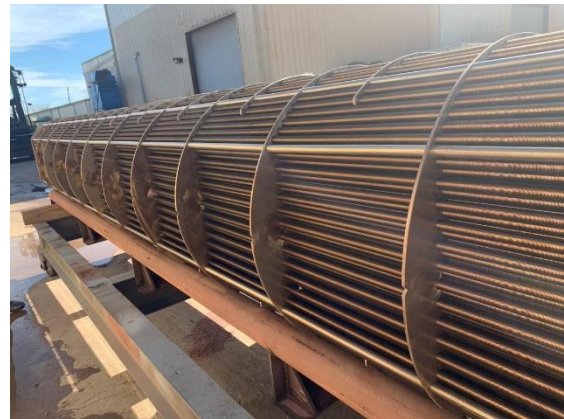


Fig. 16. Minimox-treated (shell-side and tube side, 317 SS) heat exchanger tube bundle for



hydroprocessing. To be installed in service in summer 2022.

## CONCLUSIONS

The studies presented in this paper evaluated the potential of Minimox, a novel surface treatment technology, in reducing fouling rates in process equipment used in the Oil and Gas Industry. The results, which showed great promise for fouling and CO<sub>2</sub> reduction, led to the following conclusions:

1. *Low surface energy is produced.* Several publications related low surface energy to lower fouling rates. The low surface energy of yttria is inherently related to its low work function.
2. *Low % surface polarity is manufactured.* Other publications discussed in this paper imply that low % surface polarity translates to lower fouling rates.
3. *The Minimox treatment yields a very thin layer that is integral to the alloy surface.* Consequently,

any additional thermal resistance associated with the Minimox treatment is negligible. Furthermore, the coating cannot flake off with mechanical abrasion or thermal cycling.

4. *High temperature stability.* Minimox is high-temperature stable and does not impose any temperature limitations beyond those of the base metal.

## NOMENCLATURE

RE	Rare Earth
REE	Reactive Element Effect
REOs	Rare Earth Oxides
SFE	Surface free energy, mN/m
SS	Stainless Steel
%SP	Percent Surface Polarity, = Polar Fraction of surface energy X 100/surface free energy

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