

ICAC Forum '02, February 2002

**SCR Treatment of Ethylene Furnace Flue Gas  
(A Steam-Methane Reformer in Disguise)**

Robert G. Kunz, Ph.D., P.E.

and

T. Robert von Alten

Cormetech, Inc.

Environmental Technologies

**ABSTRACT**

Come find out what Texas Gulf Coast ethylene plants have in common with a steam-methane reformer (SMR) hydrogen plant in a California refinery. As more stringent NO<sub>x</sub> control is implemented in the Houston – Galveston area, new selective catalytic reduction (SCR) units will be installed on combustion sources there, including numerous ethylene plant pyrolysis furnaces. Meanwhile, other SCRs have been operating successfully on both SMRs and ethylene plants.

SCR performance data from the two processes are explored in this presentation, following a brief description of the processes themselves and noting the similarities and differences between their process furnaces. In operating installations, an accelerated deterioration in SCR catalyst has been found to originate from the metallurgy of each type of plant, limiting the length of run before necessary catalyst replacement. A proper design requires a thorough understanding of these phenomena, and further details are given in the paper. The common culprit depositing on the catalyst surface has been identified as an oxide of chromium.

## INTRODUCTION

A number of the ethylene plants in the US<sup>1</sup> are located in ozone-nonattainment areas, and their operators are faced with having to comply with increasingly stringent emission-control limits for oxides of nitrogen (NOx). This NOx is generated in the combustion process in a boiler, heater, furnace, or combustion turbine. Naturally, the first thought to achieve a new, lower level for compliance is to turn to low-NOx burners, where the newest designs have made substantial, dramatic reductions in NOx.<sup>2</sup> However, demonstrated reductions in a multi-burner, full-scale environment are not quite good enough, it appears, to meet the latest regulatory requirements for NOx by means of burners alone. Thus has it been in California for many years now and so it is / will be in the Houston – Galveston area of the US Gulf Coast where an extensive Clean Air initiative is currently underway.<sup>3</sup>

Some sources, including ethylene plants, will turn to selective catalytic reduction (SCR) employing flow-through honeycomb modular catalysts to meet their NOx-abatement needs. Prior experience reported for SCR on ethylene plant furnaces is limited, but SCR treatment of the furnace flue gas in steam-methane reformers is a subject area where considerable in-house expertise has been accumulated. Proper design in either case will account for the presence of chromium species in the furnace flue gas, which condense on the surface of the SCR catalyst and adversely affect SCR performance and catalyst life. This presentation looks at the commonalities between the two processes and analyzes the remarkably similar experiences reported for two ethylene plants in Japan<sup>4,5</sup> and a hydrogen plant in California.<sup>6-8</sup>

## TERMINOLOGY

### Ethylene Manufacturing

The chemical reaction of hydrocarbons to produce ethylene and other olefins is accomplished at high temperature, low pressure, and very short residence times (generally less than 1 second) in flow-through tubular reactors suspended in a fuel-fired furnace.<sup>9-12</sup> When no catalyst is employed, the process is referred to as *thermal cracking* or *pyrolysis*.<sup>13,14</sup> The term *pyrolysis* refers to the decomposition of a compound by the action of heat alone. This word is taken from the Greek *pyros*, fire and *lysis*, a loosening, and hence means cleavage by heat.<sup>15</sup> In a modification called *steam cracking*,<sup>16-17</sup> the hydrocarbon is diluted with steam, heated for a fraction of a second, then rapidly cooled;<sup>14</sup> these units are commonly referred to as *steam crackers*.<sup>12</sup>

Hence, the terms for the process used to manufacture ethylene: *cracking*, *thermal cracking*, *pyrolysis*, *steam cracking*, etc. are synonymous, as are the terms for the equipment in which it is manufactured:<sup>9</sup> *cracker*, *cracking furnace*, *cracking heater*, *steam cracker*, *ethylene cracker*, *ethylene unit*, *ethylene heater*, *ethylene furnace*, and *pyrolysis furnace*.

## Hydrogen Production by Steam-Methane Reforming

There are several commercially important processes for the production of hydrogen. These are partial oxidation of hydrocarbons, coal gasification, electrolysis of water, and reaction of steam with hydrocarbons (steam reforming);<sup>18</sup> hydrogen is recovered as a by-product from other operations, such as ethylene pyrolysis and petroleum refining. The manufacturing process with the lowest cost is steam reforming when natural gas is the hydrocarbon source.<sup>18,19</sup> It is variously referred to as *steam reforming*,<sup>8,18,20-23</sup> *reforming*,<sup>8,11</sup> *catalytic steam reforming*,<sup>19</sup> *catalytic reforming of hydrocarbons*,<sup>24</sup> *methane reforming*,<sup>24</sup> *steam-methane reforming*,<sup>25</sup> and *SMR*,<sup>26</sup> and the device for carrying it out as a/an *hydrogen plant*,<sup>8</sup> *steam reformer*,<sup>21,27</sup> *reformer*,<sup>8,22,27</sup> *steam-methane reformer*,<sup>26</sup> *SMR*,<sup>26</sup> *SMR furnace*, *reformer furnace*,<sup>8</sup> *primary reformer*,<sup>8,18,19</sup> and *primary reformer furnace*.<sup>18</sup> *Primary reformer* and *primary reformer furnace* are terminology from ammonia manufacturing. In that process, the effluent from the primary reformer enters the so-called *secondary reformer*, an autothermal catalyst-filled vessel into which air is introduced to supply the required nitrogen and to provide oxygen to burn off the unconverted methane concentration prior to ammonia synthesis.<sup>20</sup>

These terms will also be considered synonymous here. They should not be confused with the *catalytic reforming* of gasoline and refinery naphthas, a petroleum refining process conducted over a platinum catalyst and involving multiple reactions such as cracking, polymerization, dehydrogenation, and isomerization to upgrade gasoline octane rating.<sup>11</sup>

## PROCESS DESCRIPTIONS

### Steam Cracking to Produce Ethylene

Steam cracking of hydrocarbon feedstocks is the primary commercial route to ethylene and its coproducts. In the steam cracking process, hydrocarbon feed is mixed with steam and passed continuously through coils heated in a furnace to obtain the desired conversion via thermal cracking (Figure 1, left). Steam is added to the hydrocarbon in the reaction mixture to minimize undesired coke formation and reduce the partial pressure of the hydrocarbon to maximize yield of gaseous olefin products.<sup>9,12,14,28</sup> The reaction mixture is then cooled and separated into its constituents. Because coke is formed inside the coils as an undesired by-product that interferes with the operation, elements of the process train must be taken out of service periodically and “decoked” using a mixture of steam and air (not shown in the figure). Hydrocarbons from ethane, propane, and butane, and LPG through naphthas and heavy gas oils can be used as feed. Liquefied petroleum gas (LPG) is a mixture of light hydrocarbons (such as propane, isobutane, and *n*-butane) obtained from petroleum refining.<sup>16</sup> A more complete process description is contained in Appendix A; flow sheets are available elsewhere.<sup>29</sup>

These plants are large users of utilities: fuel, power, and cooling water. They make use of steam-driven centrifugal compressors plus refrigeration at cryogenic temperatures to separate the light product gases.<sup>14</sup> The plant can be integrated with gas-turbine technology to generate its own power.<sup>9</sup> Naphtha and gas oil plants produce an excess of fuel over and above requirements to fire the process furnace and to provide high-pressure steam for the plant’s steam-driven compressors.<sup>14</sup>

## Steam-Methane Reforming to Produce Hydrogen

The steam-methane reforming (SMR) process makes hydrogen by reacting steam and a hydrocarbon in the presence of a nickel-based catalyst<sup>11,18,20,24</sup> (Figure 1, right). This catalyst, in the form of pellets, hollow cylinders, or similar shapes<sup>11,21,24</sup> is contained inside alloy tubes<sup>18,20,21,30-33</sup> suspended in the radiant section of a furnace and into which a mixture of steam and desulfurized feed is introduced. Feed is usually natural gas but can also be refinery gas, propane, liquefied petroleum gas (LPG), butane, and straight-run naphtha.<sup>18,21,22</sup> Further details on the SMR process can be found in Appendix B; flow sheets are also available elsewhere.<sup>34</sup>

Downstream processing (not shown) reacts additional steam to maximize the hydrogen yield, and the hydrogen product is separated from the resulting synthesis gas (syngas), a generic term for mixtures of hydrogen (H<sub>2</sub>), carbon monoxide (CO), and carbon dioxide (CO<sub>2</sub>). Hydrogen is used in petroleum refining, and hydrogen production is the first step in the manufacture of ammonia.<sup>20</sup> Hydrogen is also a coproduct in the manufacture of carbon monoxide (CO).<sup>25</sup>

As with ethylene manufacturing, this process can also be integrated with gas-turbine exhaust,<sup>26</sup> and the steam produced can be used instead of electric drive.<sup>24</sup>

## COMPARISON OF STEAM CRACKING AND STEAM-METHANE REFORMING

Important similarities and differences between the processes to manufacture ethylene and other olefins and to produce hydrogen are summarized in Table 1. Strong similarities exist on the flue-gas side, from the furnace all the way through heat recovery to the stack. Differences are reflected on the process side because different feed materials are subjected to different reaction conditions to make different products.

### Similarities

**Furnace and Burners.** Both processes make use of a furnace to supply the endothermic heat of reaction from combustion of fuels in burners installed in the radiant section. The job of the burners is to deliver the heat in a perfectly uniform manner, but to reach this ideal condition would require an infinitely large number of burners. Ethylene cracking furnaces and hydrogen reforming furnaces most closely approximate this ideal arrangement by using many small burners.<sup>35</sup>

**Fuels.** Fuels may be generated as by-products of the respective processes or may be derived from external sources (Table 2). Fuels for an ethylene furnace may include methane-rich gas (also known as the pyrolysis methane fraction), hydrogen-rich fuel gas, and pyrolysis fuel oil<sup>16</sup> (Appendix A). Fuels for a hydrogen reformer furnace may include PSA purge gas, along with supplementary fuel from an external source,<sup>18,21</sup> including the feed gas<sup>24</sup> (Appendix B). Fuels from external sources for both include natural gas, refinery gas, and distillate fuel of some sort.

**Integration with Gas Turbine Exhaust.** The burners may use ambient air or preheated air. Gas turbine exhaust can replace or supplement the combustion air.<sup>9,26</sup>

**Process Heater Coils and Tubes.** Some typical alloys used for radiant coils/heater tubes are listed in Table 3. For the most part, both ethylene plants and steam-methane reformers at the present time employ tube-metal alloys of a very similar composition containing upwards of about 25% chromium (Appendix C). Nominal composition ranges from about 25-35% chromium (Cr) and 20-45% nickel (Ni). The ethylene industry has now standardized more or less on the so-called HP-modified alloys for pyrolysis furnaces.<sup>36</sup> The most common variation adds ~1-1.5 % niobium (Nb) to the basic alloy, possibly "microalloyed" with trace quantities of titanium (Ti), zirconium (Zr), and rare earths in addition to the Nb.<sup>36-39</sup> The HP Modified Nb alloy has been adopted as a standard for steam-methane reformers as well.<sup>32</sup> The ammonia industry has used HP Modified alloys in the hydrogen plant primary reformer since the 1980s;<sup>38,39</sup> this is consistent with hydrogen-plant literature<sup>21,22</sup> and a spot sampling of hydrogen plant designers and operators.<sup>30</sup> Some IN 519 and HK-40 tubes may nonetheless still remain in steam-reforming service in older plants.<sup>40-42</sup>

**Temperatures.** Firebox temperature in an ethylene furnace is typically 1000-1200 °C (1832-2192 °F).<sup>16</sup> In a reformer furnace, flue gas exits the radiant firebox, referred to as the *bridgewall temperature*,<sup>24</sup> at 1800-1900 °F (~ 980-1040 °C),<sup>18,21</sup> although one source quotes a higher upper end, 2200 °F (~ 1200 °C).<sup>32</sup> Radiant-coil outlet temperatures in the cracking process are maintained anywhere from 700-950 °C (1292-1742 °F);<sup>9,11,14,16</sup> temperatures are higher for ethane feed than for naphthas than for gas oils.<sup>16</sup> The steam-methane reforming (SMR) reaction is close to equilibrium<sup>18,20-22,24</sup> at the reformer outlet temperature of up to about 1600 °F (871 °C).<sup>18,21</sup> Tube-metal temperatures may vary from 1750 °F to as high as the 1950-2100 °F range for ethylene plants<sup>36,36,43-46</sup> and somewhat lower in the 1600 °F to 1925 °F range for hydrogen reformers.<sup>21,24,32,41,46</sup>

**Heat Recovery.** In the ethylene cracking process, heat is recovered by generating and superheating steam and by heating the feed, boiler feed water, or other process streams<sup>9,14</sup> as the flue gas is cooled before being discharged to atmosphere. Temperatures of 170-200 °C (338-392 °F) immediately upstream of the stack have been reported.<sup>4</sup> In a steam-methane reformer, heat from the flue gas is recovered by preheating the feed, producing/superheating steam, and perhaps preheating the combustion air.<sup>18,19,24</sup> Temperature at the stack following waste heat recovery is said to be about 300 °F (~150 °C),<sup>21</sup> 200-260 °C (392-500 °F),<sup>19</sup> and 150-170 °C (302-338 °F),<sup>18</sup> depending on the type and amount of heat exchange with other fluids.

**Chromium Poisoning of SCR Catalyst.** As we shall see in the discussion below, the two processes share another point in common when SCR is used to control NOx in the furnace flue gas.

## Differences

On the process side, similarities are minimal. Feeds will most likely be different, and the presence or absence of a catalyst brings about different sets of products. Hydrogen, however, is one of several by-products of the ethylene cracking process. The processing schemes for product recovery are different as well. Operating pressures differ by an order of magnitude as does the ratio of steam to feed. Because of the difference in the amount of steam added, coke more readily forms during the cracking reactions and must be removed frequently from the inside of the

pyrolysis coils using a mixture of steam and air. SMR catalyst must be changed every few years to compensate for an expected deterioration in performance. That deterioration is hastened by any coking that may have occurred or by poisoning from sulfur compounds. Differing process conditions lead to different methods of coil/tube failure. The different by-products used as fuels, as described above, will result in somewhat different emissions to the atmosphere. Nevertheless, the flue gas from either process must undergo additional treatment for NO<sub>x</sub> removal to meet the strictest regulatory standards.

## **THE SCR PROCESS**

In this process, the oxides of nitrogen NO and NO<sub>2</sub>, commonly known as NO<sub>x</sub>, are reacted with ammonia (NH<sub>3</sub>) in the presence of a suitable catalyst to give nitrogen (N<sub>2</sub>) and water vapor (H<sub>2</sub>O)<sup>6,7</sup> (Figure 2). Aqueous or anhydrous ammonia is injected upstream of the catalyst through the so-called ammonia injection grid (AIG). Reaction stoichiometry with ammonia depends on the relative amount of each oxide and whether or not oxygen (O<sub>2</sub>) is present. For combustion applications containing excess oxygen and parts-per-million (ppm) concentrations of NO<sub>x</sub> with the typical 95 % NO and 5 % NO<sub>2</sub> split, the equations given in Figure 2 apply. In the absence of competing side reactions, the theoretical molar ratio of NH<sub>3</sub> reacted to NO<sub>x</sub> destroyed is 1.0.

## **APPLICATION OF SCR TECHNOLOGY TO ETHYLENE MANUFACTURING AND HYDROGEN PRODUCTION**

Performance of the Selective Catalytic Reduction (SCR) NO<sub>x</sub> removal process has been demonstrated on both the ethylene manufacturing process and the steam-methane reforming (SMR) process for hydrogen production. Operating conditions for these cases and other pertinent information are summarized in Table 4 and discussed further below.

### **Reported SCR Experience on Ethylene Furnaces**

Two technical papers presented at the 2001 A.I.Ch.E. Ethylene Producers' Conference describe SCR installations on ethylene plants in Japan using base-metal flow-through catalysts in the conventional temperature range.<sup>4,5</sup> The SCR catalysts in both plants met their guarantees, and each plant met the NO<sub>x</sub> requirements of its air-quality permit. Both plants are integrated with gas turbines.

According to information from the Internet, the cities of Ichihara (population 280,000) and Chiba (population 870,000), where these plants are located, are situated on the eastern shore of Tokyo Bay in the Chiba Prefecture across from the city of Tokyo. The Chiba Prefecture, one of 47 such administrative divisions of Japanese government, occupies a peninsula between Tokyo Bay and the Pacific Ocean on the east coast of Japan's Honshu Region. It encompasses an area of 1991 square miles (5156 square kilometers), with a Year 2000 population of 5.9 million. A large petrochemical complex or complexes are located in this vicinity. It is possibly because of this concentration of industry as well as the population density that the prefecture's NO<sub>x</sub> emission

limits are stricter than those of the national government<sup>4</sup> and have become even more stringent in later years.<sup>5</sup>

**Maruzen Ichihara Ethylene Plant.** The Maruzen Petrochemical Co., Ltd. naphtha cracking plant in Ichihara, Japan,<sup>5</sup> employs steam injection to its gas turbine and uses low-NOx burners in the furnace. The furnace fuel is not disclosed though it is probably a clean gaseous fuel (from the process, or natural gas) since flue-gas SOx is shown as zero. Design-basis flue-gas flow rate is 140,000 kg/hr (approx. 75,000 SCFM at 60 °F, 1 atm). The catalyst consists of 40 x 40 cells (3.75 mm pitch). Design temperature for the SCR is 290-370 °C (~550-700 °F). The plant and SCR have operated since 1994, more than 6 years.

The original design was for NOx of 100 ppmv at the SCR inlet and 30 ppmv at the outlet, both at 6 % O<sub>2</sub> (dry), a 70% NOx removal efficiency. Expression of pollutant concentrations on a dry basis at 6 % O<sub>2</sub> appears to be a Japanese regulatory standard. On a 3 % O<sub>2</sub> basis, a standard widely used in the US for boilers and fired heaters, inlet and outlet NOx would be 120 ppmvd and 36 ppmvd, respectively. The intention of either standard is to prevent the attainment of compliance simply by dilution with greater amounts of excess combustion air. At the end of the first year of operation, actual inlet NOx after the gas turbine was 74 ppmv; outlet NOx 14 ppmv and ammonia slip 5 ppmv, all at the operating condition of 4.1% O<sub>2</sub>. These figures would each be 6.5 % higher when corrected to 3 % O<sub>2</sub>.

**Idemitsu Chiba Ethylene Plant.** The Idemitsu Ethylene Plant in Chiba, Japan,<sup>4</sup> uses some vacuum gas oil (VGO) in the feed and burns all of the produced pyrolysis fuel oil as part of the furnace fuel. The resulting sulfur oxides in the flue gas originally at 80 ppmv (design) and later at 10 to 30 ppmv (actual) caused concern about plating out of ammonium sulfate and ammonium bisulfate on the downstream economizer or their becoming particulate emissions.

The SCR catalyst bed consists of five layers. From information given in the paper, it is possible to deduce that the catalyst pitch size is 7.5 mm (20 x 20 cells) and that the dry flue-gas flow rate is about 239,000 SCFM (60 °F, 1 atm). Calculated wet flue-gas flow rate at the resulting 19 % moisture concentration is about 295,000 SCFM (60 °F, 1 atm). SCR temperature was maintained between 350 and 400 °C (~660-750 °F). The plant and SCR have operated for over 15 years since 1985; SCR operating data during the most recent 5.5 years are described in greater detail. During the lifetime of the plant, two catalyst replacements have occurred, once at 6 years and again at 12 years. On each occasion, the layers in the lead positions were removed and replaced by the trailing layers, and new catalyst was installed in the trailing positions.

Original design figures were 237 ppmv inlet NOx and 86 ppmv outlet NOx, for a NOx removal efficiency of 63.7% at the design condition. Design ammonia slip was 5 ppmv or less. The unstated oxygen concentration is calculated as 2.33 %. Inlet and outlet NOx correspond to 190 ppmvd and 69 ppmvd, respectively, at 6% O<sub>2</sub>, and 229 ppmvd and 83 ppmvd at 3 % O<sub>2</sub>. After modifications were made to the gas turbine, SCR inlet NOx was measured between 140 and 180 ppmv, and outlet NOx about 80 ppmv.

#### **Reported SCR Experience on a Steam-Methane Reformer Hydrogen Plant**

Field test results of SCR performance on a hydrogen plant located at a California refinery<sup>8</sup> in the San Francisco Bay Area were presented in 1996 at an Air & Waste Management Association Annual Meeting<sup>6</sup> and were updated for publication in the Association's Journal.<sup>7</sup> This plant was not integrated with a gas turbine. The period of operation described covered 3 years.

During periodic field testing, natural gas was fed to the plant, and natural gas or refinery fuel gas was used as fuel. SCR temperature ranged from 651 to 673 °F (344-356 °C), excess O<sub>2</sub> from 3.0-3.7%, and flue-gas moisture from 14-18%. NO<sub>x</sub> removal efficiency for the compliance-demonstration runs was about 85%, and the measured outlet NO<sub>x</sub> and ammonia slip were in compliance with their permit limits of 10 and 25 ppmd at 3% O<sub>2</sub> (dry), respectively.<sup>6-8</sup> Cormetech supplied the catalyst for this installation.

### **Decline in Catalyst Activity**

For one reason or another,<sup>47</sup> the ability to catalyze the SCR reactions decreases during exposure of the catalyst to flue gas. This catalyst activity is plotted as a ratio,  $K/K_0$ , the activity at any time divided by its initial activity<sup>48</sup> (Figure 3). The ratio starts out with a value of 1.0 at time zero and gradually falls as the catalyst ages by exposure to flue gas. When its value is such that the source cannot meet its permit limits for outlet NO<sub>x</sub> and ammonia slip simultaneously, the plant must be shut down to replace the SCR catalyst. One would hope to run for a number of years before that occurs and to have the replacement coincide with a scheduled outage.

**Lower-Than-Expected Performance.** However, in the ethylene plants and the hydrogen plant under consideration, performance of the initial charge of catalyst deteriorated faster than would ordinarily be anticipated. In the Maruzen Ichihara Ethylene Plant, for example, actual deactivation to 70-80 % of initial conditions was observed after one year of operation, versus an expected deactivation of less than 10 %.<sup>5</sup>

Data points and curves as drawn in the original references are shown in the figure, along with horizontal lines denoting the minimum catalyst activity necessary for permit compliance. The curve for the Idemitsu Chiba Ethylene Plant represents the performance of the initial charge of the #1 catalyst layer, the layer located farthest upstream at the SCR inlet for the first 6 years. Catalyst activity curves published for the initial #5 layer and for the #4 layer relocated to the lead position when the #1 layer was replaced after 6 years of service are not shown in Figure 3. These both exhibit a lower rate of decay than layer #1.

Minimum required activity, or the projected end of the run, is slightly different for the Idemitsu Ethylene Plant and the hydrogen plant in California, but just above  $K/K_0 = 0.2$  for both. No minimum required activity was reported for the Maruzen plant. Its curve terminates between 0.3 and 0.4 at 6 years, accompanied by a statement that the NO<sub>x</sub> removal rate at 4 years would almost have met its guarantee of 70 %. This corresponds to a  $K/K_0$  from the curve of about 0.42. The plant's original charge of catalyst was still being used at 6 years to achieve an outlet NO<sub>x</sub> of less than 30 vppm because the actual inlet NO<sub>x</sub> was lower than the design basis.

**Chromium Deposition.** In all three plants, there turns out to be a common cause for the accelerated decline in  $K/K_0$ . Both ethylene plant papers report a premature loss of catalyst activity ascribed to chromium compounds accumulated on the catalyst surface to a depth of 20-30 microns<sup>4</sup> or to a chromium oxide mist vaporized from the radiant coils and condensed onto the catalyst surface.<sup>5</sup> The deposit is said to be chromium and iron oxides submicron in size and much smaller than the ash or coke from the combustion process.<sup>5</sup> Flue-gas concentration of Cr<sub>2</sub>O<sub>3</sub>, assumed to be vaporized in the furnace radiant section and later to condense on the catalyst surface downstream, was calculated by the authors of the Maruzen paper to be 1 part per billion (ppb) at 1000 °C (1832 °F), presumably based on vapor pressure for Cr<sub>2</sub>O<sub>3</sub>.<sup>5</sup> For the



design-basis flue-gas flow rate and other conditions reported,<sup>5</sup> this would translate into a total of 16 lb/yr (7 kg/yr) of Cr<sub>2</sub>O<sub>3</sub> or 11 lb/yr (5 kg/yr) as chromium.

Cormetech has encountered this same phenomenon in numerous hydrogen plants for which we have supplied catalyst and done extensive follow-up testing. In those plants also, the loss of catalyst activity experienced has been attributed to a masking of active catalyst surface by an ongoing deposition of some form of chromium, as noted for the Martinez, California location.<sup>7</sup> This layer is also believed to have been deposited on hydrogen-plant SCR catalyst by evaporation of chromium species from the alloy metals in contact with hot flue gas. As mentioned above, the same family of alloys is used in both ethylene plant pyrolysis/cracking furnaces and steam-methane reformer furnaces, and the tube-metal temperatures are similar (Table 3, Appendix C).

In the cases that we have seen from steam-methane reforming, this masking layer manifests itself as a discoloration of the SCR catalyst surface, heavy at the inlet and becoming gradually lighter approaching the outlet. The color deepens and spreads farther downstream with greater exposure time. The color varies from brownish to an iridescent black, possibly depending on the temperature of chromium oxide condensation on the catalyst. In Figure 4, a photograph is shown of an exposed sample removed from an unspecified SMR plant, along with a fresh, unexposed sample for comparison. The discoloration of the exposed sample (on the right) is dark brown at the inlet face and an orange-brown at the outlet (not pictured). The fresh catalyst sample shown on the left in Figure 4 is a light tan, with a nominal pitch in the range of 2-4 mm, typical of clean-gas service.

Chromium (III) oxide, chromic oxide (Cr<sub>2</sub>O<sub>3</sub>), is a green powder; insoluble in water, but preparation at high temperatures results in the crystallized state, black and iridescent with a metallic luster; the crystallized form has the same molecular-lattice structure as the mineral, corundum ( $\alpha$ -alumina, Al<sub>2</sub>O<sub>3</sub>).<sup>49</sup> The light to dark green fine hexagonal crystals are said to turn brown on heating, reverting to green on cooling [Merck Index, 12 ed., p.373].<sup>50</sup> Also, it is conceivable that the greenish hue of the lower-temperature form of chromic oxide would appear brownish on top of a tan substrate; that some reddish chromium (VI) oxide, chromium trioxide (CrO<sub>3</sub>), might be present;<sup>51</sup> or that impurities picked up along with the chromium compounds could affect the color. One such impurity could be an oxide of iron (Fe),<sup>52</sup> as mentioned for the Maruzen plant.<sup>5</sup> Black overwhelms any other color present.

### Vaporization of Cr<sub>2</sub>O<sub>3</sub> from Alloy Tubes and Coils

**Properties of Cr<sub>2</sub>O<sub>3</sub>.** Chromic oxide (Cr<sub>2</sub>O<sub>3</sub>), is a solid that melts at 2345 °C (4253 °F), begins to evaporate at 2000 °C (3632 °F) to form clouds of green smoke, and boils at an estimated 3000-4000 °C (5472-7232 °F).<sup>53</sup> At typical flue-gas and tube-metal temperatures, Cr<sub>2</sub>O<sub>3</sub> is therefore a solid,<sup>51,54</sup> not a liquid. Direct change of phase from the solid state to the vapor state is more properly termed *sublimation* rather than *evaporation*, but the terms *evaporation* and *vapor pressure* will be used interchangeably here with *sublimation* and *sublimation pressure*, respectively.

For reasons explained below, vapor pressure data for Cr<sub>2</sub>O<sub>3</sub> per se are not to be found, compared to a relative abundance of vapor pressure data for chromium metal.<sup>55-58</sup> Data for some other chromium species containing oxygen are available.<sup>59-62</sup>

**Oxide Scale.** Oxidation resistance of stainless steels and many high-temperature nickel-based alloys containing chromium is provided by protective Cr<sub>2</sub>O<sub>3</sub> surface layers that minimize diffusion of various species through them and greatly reduce the rate of further oxidation; the Cr<sub>2</sub>O<sub>3</sub> normally forms spontaneously upon exposure to oxidizing conditions at high temperatures.<sup>63</sup> Its fast initial growth also protects against attack of the metal by aggressive materials such as sulfur and chlorine.<sup>64</sup> Oxidation of the metal beneath increases sharply whenever a mechanical break in the protective covering occurs.<sup>65</sup>

At least two laboratory studies have been published containing the high-temperature oxidation behavior of commercial chromium-nickel alloys. One of these,<sup>66</sup> addresses Incoloy 800, an alloy previously used to fabricate reformer tubes and pyrolysis coils (Table 3). The subject of the other investigation<sup>67</sup> is an HP-40 Nb Mod Microalloy formulation, a present-day alloy of choice for these services (Table 3, Appendix C). A third investigation, a case history for the primary reformer of an ammonia plant, relates field experience with enhanced corrosion on the outside of catalyst tubes when firing heavy fuel oil in the furnace.<sup>68</sup>

In the first study,<sup>66</sup> three oxide layers were formed on the alloy surface during oxidation experiments of up to 100 hours at close to 1000 °C (1832 °F). The innermost layer, nearest to the metal substrate was composed of SiO<sub>2</sub>, without any chromium. The middle layer contained high Cr, thought to be indicative of Cr<sub>2</sub>O<sub>3</sub>, along with some particles of other metal oxides as impurities. The outermost layer was enriched in titanium (Ti) and Cr, a situation which was assumed to indicate a TiCr<sub>2</sub>O<sub>4</sub> spinel base, along with possibly some manganese (Mn). A spinel is a hard crystalline compound, with a structure typical of some naturally occurring minerals.<sup>69-71</sup> Spinel formation is thought to proceed according to the reaction of Cr<sub>2</sub>O<sub>3</sub> with FeO, MnO, or TiO to give FeCr<sub>2</sub>O<sub>4</sub>, MnCr<sub>2</sub>O<sub>4</sub>, or TiCr<sub>2</sub>O<sub>4</sub>.<sup>66</sup>

Oxidation kinetics was controlled by diffusion of oxygen atoms through the most resistant layer (here, SiO<sub>2</sub>) to the metal-SiO<sub>2</sub> interface and by cation diffusion through the chromic oxide. Evaporative loss of Cr was said to be impeded by the spinel overlayer. In a subsequent paper,<sup>64</sup> one of the authors of the second study summarized below,<sup>67</sup> attributes growth of a protective Cr<sub>2</sub>O<sub>3</sub> layer to diffusion along grain boundaries - inward diffusion of oxygen and outward diffusion of cations.

Although the focus of the second study<sup>67</sup> was coking and carburization in hydrocarbon cracking, the oxide film created during a 5-hr pre-oxidation cycle at 1000 °C (1832 °F) was characterized by the investigators. Oxide formation was evidenced by a weight gain of the samples during oxidation and a weight loss when the oxide layer spalled off as the samples were cooled to room temperature for weighing. This oxide layer consisted of only two sublayers, a relatively thick layer of Cr<sub>2</sub>O<sub>3</sub> closest to the metal, topped by a thin external layer consisting of a mixed manganese-iron chromate (Mn,Fe)Cr<sub>2</sub>O<sub>4</sub> spinel. No SiO<sub>2</sub> layer was reported.

Chemical analysis revealed an enrichment of Cr and Mn at the interface between the metal and the oxide layer compared to the bulk metal composition, indicating their diffusion outward during oxidation. What the authors call the *free metal surface*, the metal surface where the oxide layer spalled off during handling, was depleted in Cr and Mn and enriched in iron and nickel. The oxide layer itself contained 85 % Cr and close to 5 % each for Mn, Fe, and Ni. The authors' conclusion was that oxidation of the specimens had resulted in Cr-depleted areas in the metal surface. Laboratory tests<sup>52</sup> of other chromium-nickel alloys exhibited enhanced chromium in the retained oxide scale and in the condensed vapor from volatilization experiments.

The case history<sup>68</sup> is concerned in part with the corrosion of other high-chromium, high-nickel tube-metals (50Cr/50Ni and 35Cr/45Ni plus Ti and other ingredients) and their susceptibility to external corrosion in the absence of a corrosion inhibitor added to fuel oil containing vanadium (V), alkali metals, and high sulfur. Following a 10-month operating period with a very low inhibitor dosage rate, a thin metallic layer, said to be hard and difficult to brush off, covered the tubes. It formed bubbles on the outside of the tubes and, when pressed, revealed a clean tube-metal surface underneath. That corrosion layer contained a high percentage of chromium and nickel from the tubes and about 5 % vanadium originating from the fuel oil. No microscopic analysis was reported.

**Deficiencies of an Evaporation-Only Model.** When chromium alloys are oxidized at high temperatures in the laboratory, crystals of Cr<sub>2</sub>O<sub>3</sub> have sometimes been observed to condense in cooler parts of the apparatus,<sup>54,65</sup> confirming the possibility of vapor-phase transport. As summarized in Table 5, however, prediction of chromium loss from the furnace tubes to deposit elsewhere is not as simple a matter as it might seem. Chromium metal, for which vapor pressure data are readily available, is shielded from the flue gas by an oxide layer, and it is an oxide of chromium that is the material subject to vaporization. This oxide, however, is not pure Cr<sub>2</sub>O<sub>3</sub>.

Furthermore, an oxide such as Cr<sub>2</sub>O<sub>3</sub> undergoes what is termed an *oxidative vaporization*<sup>51,72</sup> at high temperature and reverts to its original form upon condensation.<sup>54,73</sup> This behavior is apparently quite common.<sup>73</sup> Vaporization at high temperatures was observed to occur in oxygen and was enhanced by moisture, but did not occur in argon, wet or dry.<sup>54</sup> Vaporization increases with increasing temperature<sup>54,74</sup> and with oxygen partial pressure at a given temperature.<sup>74</sup>

The Cr<sub>2</sub>O<sub>3</sub> disproportionates into products like Cr, CrO, CrO<sub>2</sub>, and molecular and atomic oxygen in the vapor phase<sup>75</sup> in the absence of oxygen from an outside source. When external oxygen is present, as in a flue gas containing excess air, CrO<sub>3</sub> is also produced,<sup>54,75</sup> and the equilibrium is shifted among the various oxide species.<sup>51,59,76</sup> With accompanying flue-gas water vapor in addition to the oxygen, gaseous hydroxides and oxyhydroxides such as CrO<sub>2</sub>(OH)<sub>2</sub>, CrO<sub>2</sub>OH, and CrO(OH)<sub>2</sub> are formed as well.<sup>59,72,76</sup> The equilibrium is also affected by the composition of the substrate present.<sup>76</sup>

Each of the resultant species exerts its own partial pressure, the sum of which might be loosely termed the *vapor pressure* of Cr<sub>2</sub>O<sub>3</sub>. This so-called vapor pressure depends on gas composition as well as on temperature, and the temperature dependence of the partial pressure for each of the constituent species in the vapor phase is different. This total pressure increases by several orders of magnitude with increasing gas-phase O<sub>2</sub> and H<sub>2</sub>O but shows a much more moderate increase with temperature.<sup>51,59,63,72,76</sup>

Identification of these chromium species by direct measurement has proven difficult.<sup>63</sup> Instead, calculations requiring thermochemical data for all participating species are typically performed to predict the distribution of products at such low partial pressures.<sup>52</sup> For example, thermodynamic calculations at 1200 °K (927 °C, 1700 °F) for a combustion effluent containing 0 % excess O<sub>2</sub> and 20 % moisture lead to a "vapor pressure" for Cr<sub>2</sub>O<sub>3</sub> of about 10<sup>-9</sup> atmospheres and therefore a concentration of about 1 part per billion (ppb) by volume in a flue gas at atmospheric pressure.<sup>59</sup> For flue gas containing 10 % each of O<sub>2</sub> and H<sub>2</sub>O at this temperature, the resulting effective vapor pressure for Cr<sub>2</sub>O<sub>3</sub> is several orders of magnitude higher, 2 x 10<sup>-6</sup>, or a concentration of 2 parts per million (ppm).<sup>59</sup>

Calculation of oxide loss from the tubes or coils by means of a vapor pressure also tacitly assumes there is a constant source of material being vaporized and that it enters the flue gas at its

maximum concentration at all times. It further assumes that this vapor pressure is a function of temperature only. These assumptions are not valid. As discussed above, a deficiency of chromium atoms exists at the metal-oxide interface, and diffusion plays an important role in the evaporation process. Diffusion within the metal and oxide layer(s) would require new chromium atoms moving from the bulk alloy to the surface to travel a longer distance outward to meet up with diffusing oxygen as time goes on, thereby slowing the rate of Cr<sub>2</sub>O<sub>3</sub> replenishment for evaporation. (This hypothesis might suggest why the Idemitsu layer #4 promoted to the lead position after 6 years of operation, as mentioned above, showed an unexplained lower rate of performance deterioration than the original layer #1 installed in the lead position when the plant and all of its pyrolysis coils were new.<sup>4</sup>) Chromium species entering the gas phase must also diffuse through a fluid-flow boundary layer surrounding the external surface of the tubes/coils,<sup>51</sup> and metal loss has been seen to vary directly with gas flow below some unknown critical velocity.<sup>77</sup>

Finally, short of testing the flue gas for chromium<sup>78</sup> upstream and downstream of the SCR, there is no way to know the collection efficiency of chromium oxides in the flue gas by SCR catalyst.

## CONCLUSIONS

As ethylene plants are faced with having to comply with increasingly stringent NO<sub>x</sub> emission-control limits, more ethylene plant operators will be turning to SCR for NO<sub>x</sub> abatement. But reported experience with SCR in ethylene plants is limited. The proper design will account for the chromium content of the furnace flue gas, as related for two ethylene plants in Japan, without the undue cost of installing an ultra-conservative amount of catalyst "just to be sure."

Chromium originating from the metallurgy in ethylene plants and steam-methane reformers is picked up on the surface of SCR catalyst installed downstream. This adversely affects SCR performance and catalyst life. It may be some time before it is truly possible to focus on the furnace coils and tubes and calculate the loss of chromium from first principles. In the meantime, however, we can rely on a body of experimental data from multiple hydrogen plants to account for chromium pickup by the SCR catalyst and its effect on catalyst performance and longevity. Additional information will be forthcoming. Stay tuned.

## ABOUT THE AUTHORS

**Robert G. Kunz** joined Cormetech, Inc. in April 2001 as Technical Project Manager. He supports sales and marketing efforts in the petroleum refining and petrochemical industries by advising on business development strategy, development of training materials, technical report writing, and evaluation of laboratory and field data.

Dr. Kunz has had extensive experience in the petroleum and chemical industries, much of which has been focused on environmental control and testing of operating plants for a wide variety of atmospheric emissions and aqueous discharges. Prior to joining Cormetech, Inc., he was an environmental engineering manager at Air Products and Chemicals, Inc., Allentown, PA, and previously held engineering positions at Esso Research and Engineering Company, Florham Park, NJ and The M.W. Kellogg Company, New York, NY.

“Dr. Bob” has earned a BChE degree in chemical engineering from Manhattan College, a PhD in chemical engineering from Rensselaer Polytechnic Institute, an MS in environmental engineering from Newark College of Engineering, and an MBA from Temple University. He has contributed numerous publications to the technical literature and is a recipient of the Water Pollution Control Federation’s Harrison Prescott Eddy Medal in recognition of noteworthy research in wastewater treatment.

He is a member of the American Institute of Chemical Engineers (AIChE), the American Chemical Society (ACS), and the Air & Waste Management Association (AWMA) and is a licensed professional engineer in Alabama, Louisiana, New Jersey, Pennsylvania, and Texas.

**T. Robert von Alten** is Manager of Project Management at Cormetech, Inc. in Durham, North Carolina. Cormetech engineers and manufactures SCR catalyst for fossil fuel plants and stationary combustion systems. Mr. von Alten’s SCR project experience ranges from large utility boiler retrofits to small demonstration units.

Before joining Cormetech, Mr. von Alten was a Research Engineer with Energy and Environmental Research Corporation, where his work focused on air pollution projects, supporting the USEPA in developing Clean Air Act regulations. Previously, he served as a Process Engineer with Exxon Chemical Corporation.

Mr. von Alten received his BS degree in Mechanical Engineering from the University of Texas.

## ACKNOWLEDGEMENT

The authors are especially grateful to Mr. George Wensell for his assistance in preparing the manuscript and slides for presentation.

**Table 1**

**Comparison of Steam Cracking and Steam-Methane Reforming**

**Similarities**

- A Furnace Supplying Radiant Heat for an Endothermic Reaction
- Many Small Burners Employed in the Furnace to Deliver Heat as Uniformly as Possible
- Same Kinds of Conventional, Externally Derived Fuel Supplies
- Possible Integration with Gas Turbine-Exhaust
- The Same Types of Alloys Used for Coils/Tubes
- Flue-Gas, Process, and Tube-Metal Temperatures (Although Ethylene Plants May Run Somewhat Hotter)
- Heat Recovery Methods to Produce/Superheat Steam, Preheat Feed and Combustion Air
- Chromium Poisoning of SCR Catalyst

**Differences**

- Feedstocks (Ethane/Propane/Butane vs. Natural Gas - Naphtha Feed Possible for Both)
- Vastly Different Product Slates
- Olefins Product-Separation More Complex
- Much Lower Operating Pressures for Steam Cracking
- Much More Steam Added for SMR
- No Catalyst Employed for Steam Cracking; Catalyst Used in SMR
- Coke Produced in Thermal Cracking
- Ethylene Plant Decoking Cycle Every Few Weeks or Months Absent in SMR
- SMR Catalyst Change Required Every Few Years
- Sulfur Tolerance: May Even Add Sulfur in Steam Cracking; Must Desulfurize SMR Feed
- Tolerance for Olefins in Feed
- Chief Failure Mode of Furnace Tubes: Carburization vs. Creep Stress Rupture Cracking
- Different Types of Internally Generated Fuels
- NO<sub>x</sub> and SO<sub>x</sub> from Pyrolysis Fuel Oil vs. Lower NO<sub>x</sub> from SMR PSA Purge Gas

**Table 2**

**Fuels Used in Ethylene Plant Pyrolysis Furnaces and SMR Furnaces**

<b>Ethylene Plant</b>	<b>SMR</b>
<b>Generated in the Process:</b>	
Methane-Rich Gas (Pyrolysis Methane Fraction)	PSA Purge Gas
Hydrogen-Rich Fuel Gas	A Portion of the Feed Gas
By-Product Ethane	
By-Product Propane	.
Pyrolysis Fuel Oil	
<b>From External Sources:</b>	
Natural Gas	Natural Gas.
Refinery Fuel Gas	Refinery Fuel Gas .
Distillate Fuel Oil	Distillate Fuel Oil

Sources: Ullmann's Encyclopedia, 5 ed., Volume A 10, pp.66, 78 (1987);<sup>16</sup> Kirk-Othmer Encyclopedia, 4 ed., Volume 13, p.856 (1995);<sup>18</sup> Tindall and King (July 1994);<sup>21</sup> Ullmann's Encyclopedia, 5 ed., Volume A 13, p.328 (1989).<sup>24</sup>

**Table 3**

**Typical Alloys Used for Ethylene Plant Pyrolysis Coils and SMR Catalyst Tubes**

Alloy Designation	Weight Percent					
	Cr	Ni	C	Si	Mn	Other Elements
ACI* HK-40, 25Cr/20Ni (Previous Standard)	25	20	0.4-0.5	1.5(min)	1.5	--
ACI* HP-40, 25Cr/35Ni (Others: HP-45, HP-50)	25	35	0.4-0.5	1.5(min)	2.0	--
HP (NbMod), 36 X, 25Cr/35Ni Nb	25	35	0.4-0.5	1.5(min)	1.5-2	Nb 1-1.5
HP (Microalloy)	25	35	0.45	1.5	0.7	Nb, W, Ti, Zr, Rare Earths
28Cr/35Ni WCo, Supertherm	28	35	0.50	1.20	1.20	W 5.5, Co 15
35Cr/45Ni	35	45	0.4	1.5-2	unknown	Nb 1+, Others
NA 22 H**	28	48	0.45	1.50	1.50	W 5.0
IN 519 (for H <sub>2</sub> Reformers) (Possibly still in older units)	24	24	0.4	1.5	1.50	Nb 1.5
<b>Historical:</b>						
AISI*** Type 304 SS	18.0- 20.0	8.0- 10.5	0.08	1.00	2.00	P 0.045, S 0.03
AISI*** Type 310 SS	24.0- 26.0	19.0- 22.0	0.25	1.00	2.00	P 0.045, S 0.03
Incoloy Alloy 800	20	32	0.05	0.35	0.75	Al + Ti ≤ 0.7
Incoloy Alloy 800 H	20	32	0.1	0.5 (max)	1.50	Al + Ti ≥ 0.85

Note: Different alloys are used for other areas in the furnace.



Additional Notes to Table 3:

- \* Steel Founders Society of America (formerly Alloy Casting Institute), Des Plaines, IL.
- \*\* Used for suspension devices and shackles.
- \*\*\* American Iron and Steel Institute, Washington, DC.

Sources: Drawn from a consensus of Table 7 on p.125 of Reference [14], (McKetta and Cunningham, 1984); Figure 2 and p.98 of Reference [37], (Wysiekierski, Fisher, and Schillmoller, Jan. 1999); Figure 6 of Reference [36], (Parks and Schillmoller, Mar. 1996); Table 1 of Reference [44], (Schillmoller, Sept. 1985); Table 1 of Reference [45], (Moller and Warren, 1981); Table 1 on p.55 of Reference [46], (Schillmoller and van den Bruck, Dec. 1984); Table II of Reference [79], (Redmond and Miska, 1982); Table 1 of Reference [80], (Schillmoller, Jan. 6, 1986); Table 1 and Figure 4 of Reference [38], (Parks and Schillmoller, Oct. 1997); Table 1 and Figure 4 of Reference [39], (Parks and Schillmoller, 1997); Table 1 of Reference [81], (Dejaeger, Guns, and Korkhaus, 1995); Table 1 of Reference [40], (Shibasaki, Mohri, and Takemura, 1995); Table 2 of Reference [82], (Nair, Jan. 2001); pp.37 and 40 of Reference [41], Hamza, 1992); and p.179 of Reference [20], McKetta, Volume 47, 1994).

**Table 4**

**Summary of Case Information**

Type of Plant	Ethylene Plant <sup>5</sup>	Ethylene Plant <sup>4</sup>	Hydrogen Plant <sup>6-8</sup>
Owner	Maruzen Petrochemical Co. Ltd.	Idemitsu Petrochemical Co. Ltd.	Air Products and Chemicals, Inc.
Plant Location	Ichihara, Japan	Chiba, Japan	Martinez, California, USA
Supplier of SCR Catalyst (C) or Technology (T)	Hitachi Zosen Corp. (C)	Mitsui (MES) (T)	Cormetech, Inc. (C)
Integrated with Gas Turbine	Yes	Yes	No
Flue-Gas Flow Rate	140,000 kg/hr (wet) ~75,000 SCFM (60 °F and 1 atm)	SCFM: ~239,000 (dry), ~295,000 (wet) @ 19% H <sub>2</sub> O (60 °F, 1 atm) calc	not stated
O <sub>2</sub> dry	4.1 % (test results) 1.64 % (design basis)	2.33 % (calculated from design-basis information)	3.0-3.7 % (avg. 3.4 %) (test results)
H <sub>2</sub> O	20.9 % (design basis)	not stated; 19 % can be calc from info in paper.	14-18 % (avg. 16 %) (test results)
SCR Temperature	290-370 °C (design) (~550-700 °F)	380 °C, 716 °F (design) 350-400 °C (actual) (~660-750 °F)	651-673 °F (344-356 °C) (test results)
Ammonia Feed	Aqueous	not stated	Aqueous
Feed to Plant	Naphtha	Vacuum Gas Oil (VGO) + Others	Natural Gas
Fuels	not stated, but most likely sulfur-free gas	All of pyrolysis fuel oil produced provides part of the heat duty.	Natural Gas Refinery Fuel Gas
NO <sub>x</sub> Removal Efficiency	70 % (design) 81 % (actual)	63.7 % (design) ~40-60 % (actual)	~85 % (compliance- demonstration runs)
Outlet NO <sub>x</sub> at 6 % O <sub>2</sub> dry Outlet NO <sub>x</sub> at 3 % O <sub>2</sub> dry* (ppmd)	30 (design) 36 (design) 14.9 test at 4.1 % O <sub>2</sub>	69 (design) 82.9 (design) 86 design at conditions	-- permit limit: 10 --
NH <sub>3</sub> slip at 6 % O <sub>2</sub> dry NH <sub>3</sub> slip at 3 % O <sub>2</sub> dry (ppmd)	25 (design) 26.6 (design) 5 test at 4.1 % O <sub>2</sub>	4 (design) 4.8 (design) 5 design at conditions	-- permit limit: 25 --
NH <sub>3</sub> /NO <sub>x</sub> molar ratio	0.83 (actual)	0.651 (design)	0.8+ (compliance- demonstration runs)
Start-up Date	Nov. 1994	June 1985	Nov. 1993
Operating Period Described	6 years	over 15 years	3 years

\* Expressing pollutant concentrations on a dry basis at a standard condition of 3% O<sub>2</sub> (dry) in the flue gas is a typical requirement in permits issued by US regulatory agencies for fired heaters.

**Table 5**

**Prediction of Chromium on Catalyst**

**Prediction of Chromium Loss from Furnace Tubes/Coils Is Not Straightforward:**

- Chromium Metal Is Shielded by a Layer of  $\text{Cr}_2\text{O}_3$ .
- $\text{Cr}_2\text{O}_3$  Is the Species Subject to Vaporization.
- However, the Solid Phase Is Not Pure  $\text{Cr}_2\text{O}_3$ .
- $\text{Cr}_2\text{O}_3$  Disproportionates in the Vapor Phase.
- “Vapor Pressure” of  $\text{Cr}_2\text{O}_3$  Depends on Flue-Gas  $\text{O}_2$  and  $\text{H}_2\text{O}$  as well as on Temperature.
- Assumption Of Constant Evaporation/Sublimation During Tube Life May Not Be Valid.
- Mass Transfer Depends on Diffusion, Fluid-Flow Boundary Layer, and Gas Velocity.
- Collection Efficiency of  $\text{Cr}_2\text{O}_3$  on SCR Catalyst Is Unknown.

**Better to Rely on Chromium Pickup Data from SMR Plants:**

- Body of Data Exists.

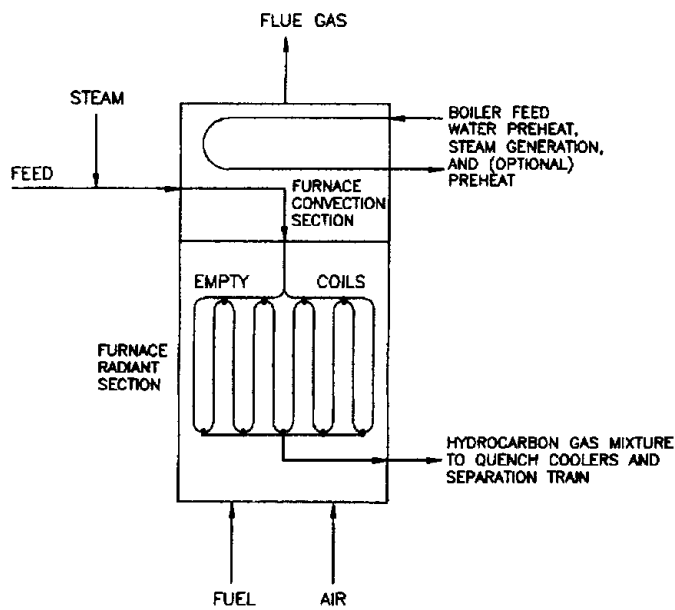
**Figure 1**

**Left: Ethylene Pyrolysis Furnace Process Flow Diagram**

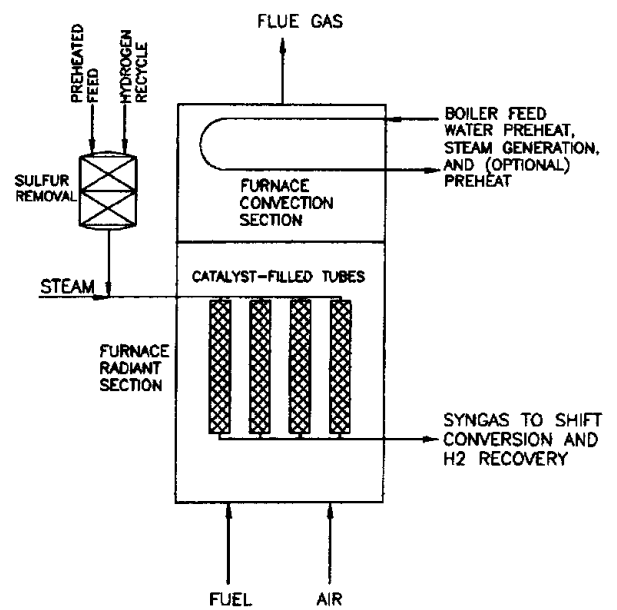
**Right: Steam-Methane Reformer Process Flow Diagram**

Figure 1

ETHYLENE PYROLYSIS FURNACE

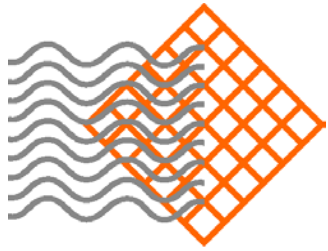


STEAM-METHANE REFORMER FURNACE



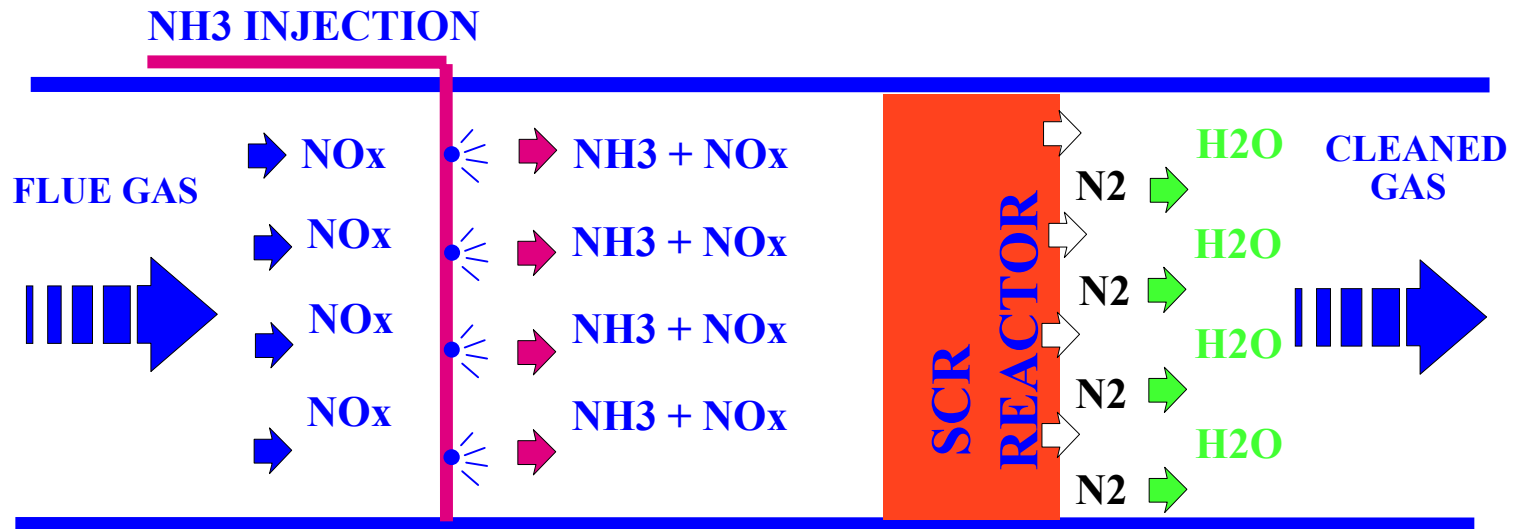
**Figure 2**

**SCR Reaction Chemistry**



CORMETECH

# SCR Reaction Chemistry



**Figure 3**

**Decline in SCR Catalyst Activity**

Sources of Data: Figure 6 on p.32 of Reference [7], (Kunz, 1998); Figure 8 on p.771 of Reference [4], (Suwa, 2001); Figure 6 on p.755 of Reference [5], (Funahashi et al., 2001).



# DECLINE IN SCR CATALYST ACTIVITY DATA AND CURVES FROM LITERATURE SOURCES

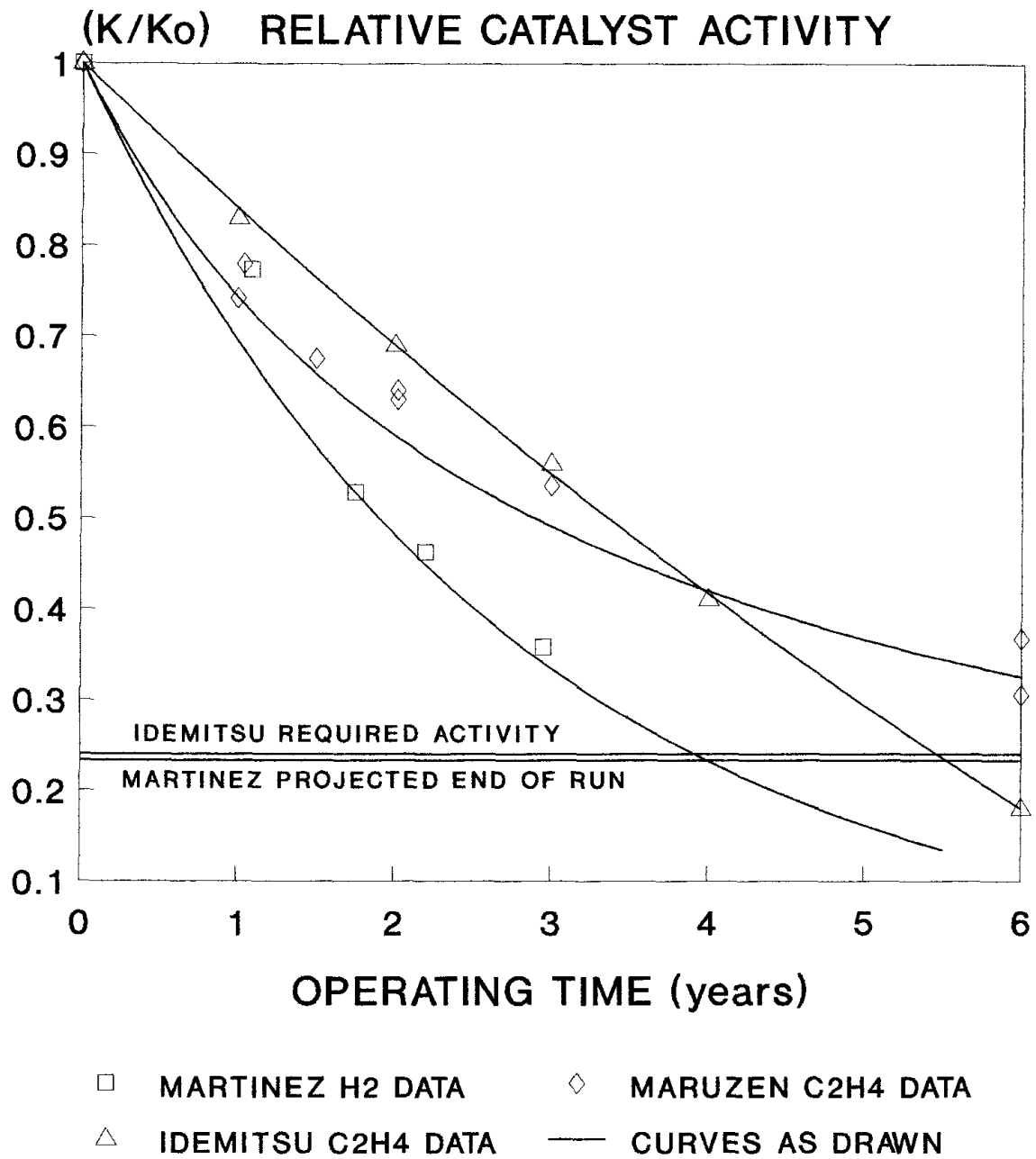


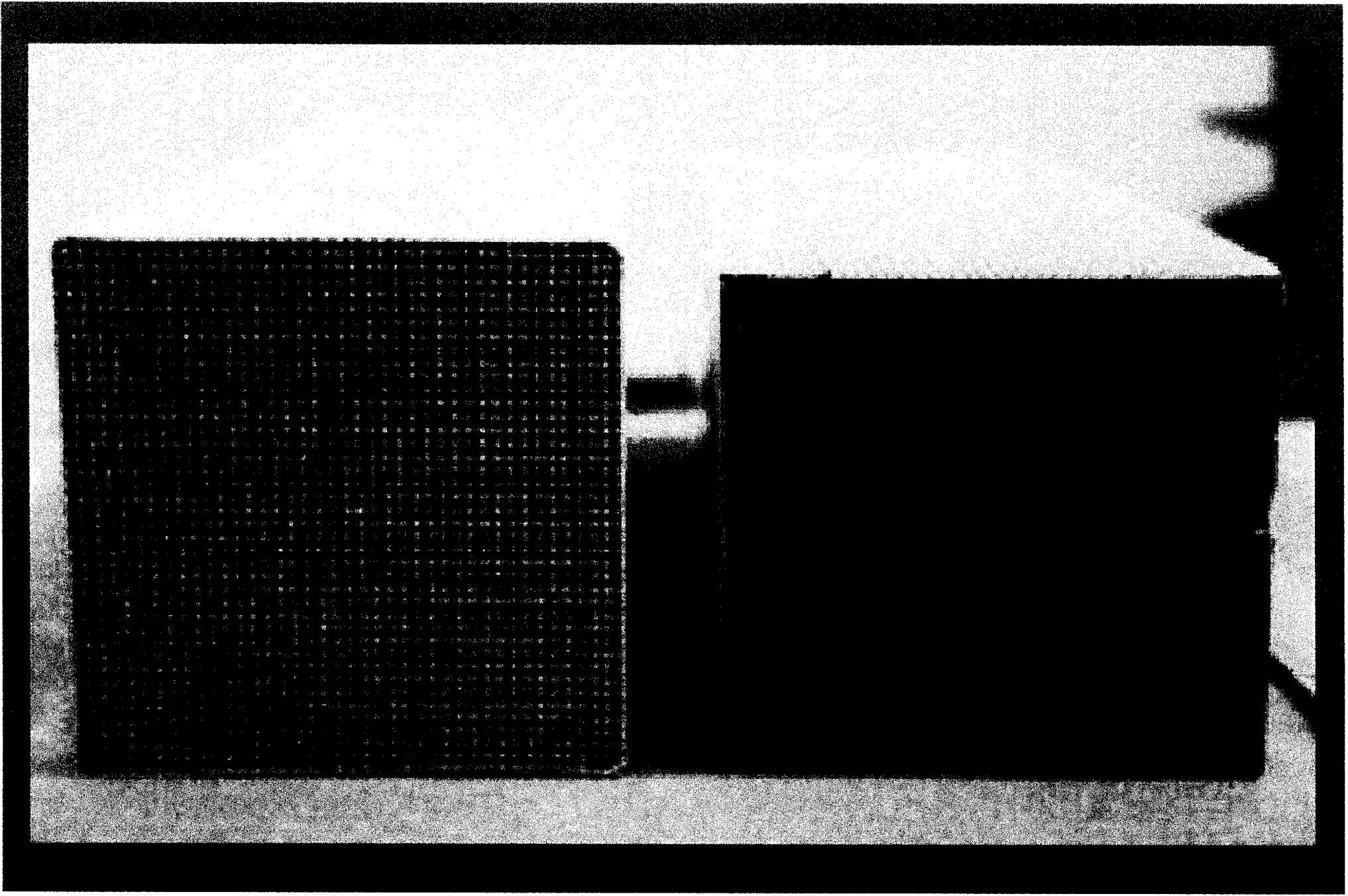
Figure 3

**Figure 4**

**Photograph of SCR Catalyst Samples**

**Left: Fresh Sample**

**Right: Exposed Sample**



## REFERENCES

1. Chang, T., "FOCUS: Ethylene," *Oil & Gas Journal*, **98(14)**, 56-67 (April 3, 2000).
2. Bussman, W., R. Poe, B. Hayes, J. McAdams, and J. Karan, "Low NO<sub>x</sub> Burner Technology for Ethylene Cracking Furnaces," *Proceedings of the 13<sup>th</sup> Ethylene Producers' Conference*, Vol. 10, pp.774-796, American Institute of Chemical Engineers, New York, NY (2001).
3. Deason, D., "Overview of NO<sub>x</sub> Reduction Issues of Concern to Ethylene Producers," *Proceedings of the 13<sup>th</sup> Ethylene Producers' Conference*, Vol. 10, pp.741-755, American Institute of Chemical Engineers, New York, NY (2001).
4. Suwa, A. "Operating Experiences of SCR DeNO<sub>x</sub> Unit in Idemitsu Ethylene Plant," *Proceedings of the 13<sup>th</sup> Ethylene Producers' Conference*, Vol. 10, pp.766-773, American Institute of Chemical Engineers, New York, NY (2001).
5. Funahashi, K., T. Kobayakawa, K. Ishii, and H. Hata, "SCR DeNO<sub>x</sub> in New Maruzen Ethylene Plant," *Proceedings of the 13<sup>th</sup> Ethylene Producers' Conference*, Vol. 10, pp.741-755, American Institute of Chemical Engineers, New York, NY (2001).
6. Kunz, R.G., "SCR Performance on a Hydrogen Reformer Furnace – A Comparison of Initial and First- and Second-Year Anniversary Emissions Data, Paper No. 96-RA 120.01 presented at the 89<sup>th</sup> Annual Meeting Air & Waste Management Association, Nashville, TN (June 23-28, 1996).
7. Kunz, R.G., "SCR Performance on a Hydrogen Reformer Furnace, *Journal of the Air & Waste Management Association*, **48**, 26-34 (1998).
8. Patel, N.M., R.A. Davis, N. Eaton, D.L. Carlson, F. Kessler, and V. Khurana, "'Across-the-Fence' Hydrogen Plant Starts up at California Refinery," *Oil & Gas Journal*, **92(40)**, 54-61 (Oct. 3, 1994).
9. Sundaram, M., et al., editors, "Kirk-Othmer Encyclopedia of Chemical Technology," 4 ed., Vol. 9, pp.877-915, Wiley, New York (1994).
10. McMurry, J., "Organic Chemistry," p.123, Brooks/Cole, Monterey, CA (1984).
11. Gary, J.H. and G.E. Handwerk, "Petroleum Refining: Technology and Economics," 4 ed., pp.189-214, 261-262, 266, 313-314, Marcel Dekker, New York (2001).
12. Royal Dutch/Shell, "The Petroleum Handbook," 6 ed., p.284, 309, 586, 689, Elsevier, Amsterdam (1983).
13. Conant, J.B. and A.H. Blatt, "The Chemistry of Organic Compounds," pp.84-85, Macmillan, New York (1952).

14. McKetta, J.J. and W.A. Cunningham, editors, "Encyclopedia of Chemical Processing and Design," Vol. 20, pp.88-159, Marcel Dekker, Inc., New York (1984).
15. Morrison, R.T. and R.N. Boyd, "Organic Chemistry," 4 ed., pp.116-117, Allyn and Bacon, Boston (1983).
16. Gerhartz, W., et al., editors, "Ullmann's Encyclopedia of Industrial Chemistry," 5 ed., Vol. A 10, pp.45-93, VCH Publishers, New York (1987).
17. Bland, W.F. and R.L. Davidson, editors, "Petroleum Processing Handbook," Section 14, pp. 14-1 to 14-46, McGraw-Hill, New York (1967).
18. Kroschwitz, J.I. and M. Howe-Grant, editors, "Kirk-Othmer Encyclopedia of Chemical Technology," 4 ed., Vol. 13, pp.838-894, Wiley, New York (1995).
19. Grayson, M. and D. Eckroth, editors, "Kirk-Othmer Encyclopedia of Chemical Technology," 3 ed., Vol. 12, pp.950-982, Wiley, New York (1980).
20. McKetta, J.J., editor, "Encyclopedia of Chemical Processing and Design," Vol. 47, pp.165-203, Marcel Dekker, Inc., New York (1994).
21. Tindall, B.M. and D.L. King, "Designing Steam Reformers for Hydrogen Production," *Hydrocarbon Processing*, **73**(7), 69-74 (July 1994).
22. Johansen, T., K.S. Ragharaman, and L.A. Hackett, "Trends in Hydrogen Plant Design," *Hydrocarbon Processing*, **71**(8), 119-127 (Aug. 1992).
23. Stoll, R.E. and F. von Linde, "Hydrogen – What Are the Costs?," *Hydrocarbon Processing*, **79**(12), 42-46 (Dec. 2000).
24. Elvers, B., S. Hawkins, M. Ravenscroft, and G. Schulz, editors, "Ullmann's Encyclopedia of Industrial Chemistry," 5 ed., Vol. A 13, pp.317-328, 435-438, VCH Publishers, New York (1989).
25. Gunardson, H.H., and J. M. Abrardo, "Produce CO-Rich Synthesis Gas," *Hydrocarbon Processing*, **78**(4), 87-93 (Apr. 1999).
26. Terrible, J., G. Shahani, C. Gagliardi, W. Baade, R. Bredehoft, and M. Ralston, "Consider Using Hydrogen Plants to Cogenerate Power Needs," *Hydrocarbon Processing*, **78**(12), 43-53 (Dec. 1999).
27. Hohmann, F.W., "Improve Steam Reformer Performance," *Hydrocarbon Processing*, **75**(3), 71-74 (Mar. 1996).
28. Hobson, G.D., editor, "Modern Petroleum Technology," 5 ed., Part II, pp. 645-651, Wiley, Chichester (1984).
29. Anon., "Special Report: Petrochemical Processes 2001," *Hydrocarbon Processing*, **80**(3), 98-102 (Mar. 2001).

30. Anon., "NPRA Q&A 1993" Ques. 2 (obtained from web site <http://www.heatflux.com>).
31. Schillmoller, C.M., "Consider These Alloys for Ammonia Plant Retrofit," *Hydrocarbon Processing*, **65(9)**, 63-65 (Sept. 1986).
32. Avery, R.E. and C.M. Schillmoller, "Repair Welding High Alloy Furnace Tubes," *Hydrocarbon Processing*, **67(1)**, 43-45 (Jan. 1988).
33. Jaske, C.E., F.A. Simonen, and D.B. Roach, "Predict Reformer Furnace Tube Life," *Hydrocarbon Processing*, **62(1)**, 63-68 (Jan. 1983).
34. Anon., "Gas Processes 2000: A Special Report," *Hydrocarbon Processing*, **79(4)**, 73-75 (Apr. 2000).
35. Baukal, C.E., Jr., and R.E. Schwartz, editors, "The John Zink Combustion Handbook," p.111, CRC Press, Boca Raton, FL (2001).
36. Parks, S.B. and C.M. Schillmoller, "Use Alloys to Improve Ethylene Production," *Hydrocarbon Processing*, **75(3)**, 53-61 (Mar. 1996).
37. Wysiekierski, A.G., G. Fisher, and C.M. Schillmoller, "Control Coking for Olefins Plants," *Hydrocarbon Processing*, **78(1)**, 97-100 (Jan. 1999).
38. Parks, S.B. and C.M. Schillmoller, "Improve Alloy Selection for Ammonia Furnaces," *Hydrocarbon Processing*, **76(10)**, 93-98 (Oct. 1997).
39. Parks, S.B. and C.M. Schillmoller, "Update in Alloy Selection for Ammonia Furnaces," *Ammonia Plant Safety & Related Facilities: a Technical Manual*, Vol. 37, pp.220-227, American Institute of Chemical Engineers, New York, NY (1997).
40. Shibasaki, T., T. Mohri, and K. Takemura, "Remaining Life Assessment of Nb-Containing Catalyst Tubes," *Ammonia Plant Safety & Related Facilities: a Technical Manual*, Vol. 35, pp.163-174, American Institute of Chemical Engineers, New York, NY (1995).
41. Hamza, M.M., "Monitoring and Replacing IN 519 Catalyst Tubes of Steam Reformer," *Ammonia Plant Safety and Related Facilities: a Technical Manual*, Vol. 32, pp.36-51, American Institute of Chemical Engineers, New York, NY (1992).
42. McKetta, J.J., editor, "Encyclopedia of Chemical Processing and Design," Vol. 47, pp.165-203, Marcel Dekker, Inc., New York (1994).
43. Anon., "NPRA Q&A 1995," Ques. 12 (obtained from web site <http://www.heatflux.com>).
44. Schillmoller, C.M., "Use These Materials to Retrofit Ethylene Furnaces," *Hydrocarbon Processing*, **64(9)**, 101-104 (Sept. 1985).
45. Moller, G.E. and C.W. Warren, "Survey of Tube Experience in Ethylene and Olefins Pyrolysis Furnaces: T-5B-6 Task Group Preliminary Report," *Materials Performance*, **20(10)**, 27-37 (Oct. 1981).

46. Schillmoller, C.M. and U.V. van den Bruck, "Furnace Alloys Update," *Hydrocarbon Processing*, **63**(12), 55-59 (Dec. 1984).
47. Pritchard, S.G., C.E. DiFrancesco, S.Kaneko, N. Kobayashi, K.Suyama, and K. Iida, "Optimizing SCR Catalyst Design and Performance for Coal-Fired Boilers," Paper presented at EPA/EPRI Joint Symposium on Stationary Combustion NO<sub>x</sub> Control (May 16-19, 1995).
48. DiFrancesco, C.E., "Quality Assurance of Catalysts During the Life of SCR Systems Through Periodic Laboratory Performance Testing," Paper presented at ACS Conference Symposium on Environmental Catalyst, Denver, CO (Apr. 1, 1993).
49. Remy, H., "Treatise on Inorganic Chemistry," translated by J.S. Anderson, F.R.S., edited by J. Kleinberg, Volume II, pp.134-135, Volume I, p.351, Elsevier, Amsterdam (1956).
50. Budavari, S., M.J. O'Neil, A. Smith, P.E. Heckelman, and J.F. Kinneary, editors, "The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals," 12 ed., p.373, Merck & Co., Inc., Whitehouse Station, NJ (1996).
51. Stearns, C.A., F.J. Kohl, and G.C. Fryburg, "Oxidative Vaporization Kinetics of Cr<sub>2</sub>O<sub>3</sub> in Oxygen from 1000° to 1300 °C," *Journal of the Electrochemical Society*, **121**(7), 945-951 (1974).
52. Zaplatynsky, I., "Volatilization of Oxides During Oxidation of Some Superalloys at 1200 °C," *Oxidation of Metals*, **11**(6) 289-305 (1977).
53. "Ullmann's Encyclopedia: Industrial Inorganic Chemicals and Products," Vol. 2, 1350-1357, Wiley-VCH, Weinheim (1998-1999).
54. Caplan, D. and M. Cohen, "The Volatilization of Chromium Oxide," *Journal of the Electrochemical Society*, **108**(5), 438-442 (1961).
55. Lide, D.R., editor-in-chief, "CRC Handbook of Chemistry and Physics," 82 ed., pp.4-134 to 4-136, 6-65 to 6-67, CRC Press, Boca Raton, FL (2001).
56. Perry, R.H., D.W. Green, and J.O. Maloney, editors, "Perry's Chemical Engineers' Handbook," 7 ed., p.2-58, McGraw-Hill, New York (1997).
57. Novy, R.F., "Atmospheres for Heat-Treating Stainless Steels," Chapter 33 in "Handbook of Stainless Steels," by D. Peckner and I.M. Bernstein, p.33-8, McGraw-Hill, New York (1977).
58. Nesmeyanov, A.N., "Vapor Pressure of the Chemical Elements," edited by R. Gary, pp.332, 454, Elsevier, Amsterdam (1963).
59. Ebbinghaus, B.B., "Thermodynamics of Gas Phase Chromium Species: The Chromium Oxides, the Chromium Oxyhydroxides, and Volatility Calculations in Waste Incineration Processes," *Combustion and Flame*, (**93**), 119-137 (1993).
60. Ebbinghaus, B.B., "Thermodynamics of Gas Phase Chromium Species: The Chromium Chlorides, Oxychlorides, Fluorides, Oxyfluorides, Hydroxides, Oxyhydroxides, Mixed Oxyfluorochlorohydroxides, and Volatility Calculations in Waste Incineration Processes," *Combustion and Flame*, (**101**), 311-338 (1995).

61. Chizhikov, D.M., Yu.V. Tsvetkov, E.K. Kazenas, and V.K. Tagirov, "Vapour Composition and Pressure of Chromic Oxide by Mass Spectrometry," *Russian Journal of Physical Chemistry*, **46(3)**, 468 (1972).
62. McDonald, J.D. and J.L. Margrave, "Mass Spectrometric Studies at High Temperatures XVI. Sublimation and Vaporization of Chromium Trioxide," *Journal of Inorganic and Nuclear Chemistry*, **30**, 665-667 (1968).
63. Bailey, J., "Volatile Cr Contamination Reduction in Atmospheric Pressure Chemical Vapor Deposition Systems by Selective Alloy Oxidation," *Journal of the Electrochemical Society*, **144(10)**, 3568-3571 (1997).
64. Grabke, H.J., "Surface and Interface Segregation in the Oxidation of Metals," *Surface and Interface Analysis*, **30**, 112-119 (2000).
65. Caplan, D. and M. Cohen, "High Temperature Oxidation of Some Iron-Chromium Alloys," *Journal of Metals*, **4(10)**, 1057-1065 (1952).
66. Fritscher, K. and Y.T. Lee, "Effect of Water Vapor on Oxidation and Creep Behavior of Incoloy 800 at Temperatures Between 850 and 980 °C," *Oxidation of Metals*, **32(3/4)**, 295-316 (1989).
67. Steurbratt, C., H.J. Grabke, D. Stobbe, F.R. van Buren, S.J. Korf, and J. Defrancq, "Kinetic Studies of Coke Formation and Removal on HP40 in Cycled Atmospheres at High Temperatures," *Materials and Corrosion*, **49**, 352-359 (1998).
68. Pequeno, C. and M. Severin, "Experiences with Heavy Fuel-Oil Firing in a Steam Reformer," *Ammonia Plant Safety & Related Facilities: a Technical Manual*, Vol. 39, pp.231-240, American Institute of Chemical Engineers, New York, NY (1999).
69. Brown, C.D., "Dictionary of Metallurgy," p.211, Wiley, Chichester (1998).
70. Merriman, A.D., "A Concise Encyclopedia of Metallurgy," p.982, American Elsevier, New York (1965).
71. Morris, L.A., "Resistance to Corrosion in Gaseous Atmospheres," Chapter 17 in "Handbook of Stainless Steels," by D. Peckner and I.M. Bernstein, pp.17-3 to 17-4, McGraw-Hill, New York (1977).
72. Fryburg, G.C., F.J. Kohl, and C.A. Stearns, "Enhanced Oxidative Vaporization of Cr<sub>2</sub>O<sub>3</sub> and Chromium by Oxygen Atoms," *Journal of the Electrochemical Society*, **121(7)**, 952-959 (1974).
73. Porter, R.F., "High Temperature Vapor Species," Chapter 3 in "High-Temperature Materials and Technology," edited by I.E. Campbell and E.M. Sherwood, pp.56-77, Wiley, New York (1967).
74. Warshaw, I. And M.L. Keith, "Solid Solution and Chromium Oxide Loss in Part of the System MgO-Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>," *Journal of the American Ceramic Society*, **37(4)**, 161-168 (1954).



75. Grimley, R.T., R.P. Burns, and M.G. Inghram, "Thermodynamics of the Vaporization of Cr<sub>2</sub>O<sub>3</sub>: Dissociation Energies of CrO, CrO<sub>2</sub>, and CrO<sub>3</sub>," *Journal of Chemical Physics*, **34**(2), 664-667 (1961).
76. Hilpert, H., D. Das, M. Miller, D.H. Peck, and R. Weiß, "Chromium Vapor Species over Solid Oxide Fuel Cell Interconnect Materials and Their Potential for Degradation Processes," *Journal of the Electrochemical Society*, **143**(7), 3642-3647 (1996).
77. Wilms, G.R. and T.W. Rea, "Loss of Metal from Chromium at Elevated Temperatures in Air," *Journal of the Less-Common Metals*, **1**(5), 411-412 (1959).
78. U.S. Environmental Protection Agency, "Compilation of Air Pollution Emission Factors, Vol. 1: Stationary Point and Area Sources," in *AP-42*, 4 ed., Table 1.4-5 on p.1.4-8 of October 1996 Supplement, U.S. Environmental Protection Agency, Research Triangle Park, NC (1985).
79. Redmond, J.D. and K.H. Miska, "The Basics of Stainless Steels," *Chem. Eng.*, **89**(21), 79-93 (Oct. 18, 1982).
80. Schillmoller, C.M., "Solving High-Temperature Problems in Oil Refineries and Petrochemical Plants," *Chem. Eng.*, **93**(1), 83-87 (Jan. 6, 1986).
81. Dejaeger, J., L. Guns, and J. Korkhaus, "Experiences with Alloy 800 H in Ammonia Plants," *Ammonia Plant Safety & Related Facilities: a Technical Manual*, Vol. 35, pp.134-144, American Institute of Chemical Engineers, New York, NY (1995).
82. Nair, M.P.S., "Control Corrosion Factors in Ammonia and Urea Plants," *Hydrocarbon Processing*, **80**(1), 85-93 (Jan. 2001).
83. Grayson, M., et al., editors, "Kirk-Othmer Encyclopedia of Chemical Technology," 3 ed., Vol. 9, pp.393-430, Wiley, New York (1980).
84. Chen, J. and M.J. Maddock, "How Much Spare Heater for Ethylene Plants," *Hydrocarbon Processing*, **52**(5), 147-150 (May 1973).
85. Sowers, G. and C. Reed, "Dynamic Optimization of Ethylene Furnaces Cracking Propane," *Proceedings of the 13<sup>th</sup> Ethylene Producers' Conference*, Vol. 10, pp.366-405, American Institute of Chemical Engineers, New York, NY (2001).
86. Kurlekar, A. and G.T. Bayer, "Enhance Furnace Tube Resistance to Carburization and Coke Formation," *Hydrocarbon Processing*, **80**(1), 80-84 (Jan. 2001).
87. Kunz, R.G., D.D. Smith, and E.M. Adamo, "Predict NO<sub>x</sub> from Gas-Fired Furnaces," *Hydrocarbon Processing*, **75**(11), 65-79 (Nov. 1996).
88. Kunz, R.G., D.D. Smith, N.M. Patel, G.P. Thompson, and G.S. Patrick, "Control NO<sub>x</sub> from Furnaces," *Hydrocarbon Processing*, **71**(8), 57-62 (Aug. 1992).
89. 40 CFR 60, Appendix A, Method 19, U.S. Government Printing Office, Washington, DC (July 1, 1995).

90. Anon., "NPRA Q&A 1995," Ques. 7 (obtained from web site <http://www.heatflux.com>).
91. Kunz, R.G. and W.F. Baade, "Predict Contaminant Concentrations in Deaerator-Vent Emissions," *Hydrocarbon Processing* (International Edition), **80(6)**, 100-A to 100-O (June 2001).
92. Fisher, B.R., "Combustion System for Primary Reformers," *Ammonia Plant Safety & Related Facilities: a Technical Manual*, Vol. 41, pp.303-313, American Institute of Chemical Engineers, New York, NY (2001).
93. Hendrix, D.E., "Cast Tube Alloy Performance in an Ethylene Pyrolysis Test Heater," *Materials Performance*, **38(6)**, 66-71 (June 1999).

## APPENDIX A

### PROCESS DESCRIPTION FOR STEAM CRACKING TO PRODUCE ETHYLENE

#### Overview

**Overview.** Steam cracking of hydrocarbon feedstocks is the primary commercial route to ethylene and its coproducts. In the steam cracking process, hydrocarbon feed is mixed with steam and passed continuously through coils heated in a furnace to obtain the desired conversion via thermal cracking (Figure 1, left). The reaction mixture is then cooled and separated into its constituents. Because coke is formed inside the coils as an undesired by-product that interferes with the operation, elements of the process train must be taken out of service periodically and “decoked”. Hydrocarbons from ethane, propane, and butane, and LPG through naphthas and heavy gas oils can be used as feed. Liquefied petroleum gas (LPG) is a mixture of light hydrocarbons (such as propane, isobutane, and *n*-butane) obtained from petroleum refining [16, p.46].

These plants are large users of utilities: fuel, power, and cooling water. They make use of steam-driven centrifugal compressors plus refrigeration at cryogenic temperatures to separate the light product gases [14, p. 92]. The plant can be integrated with gas-turbine technology to generate its own power [9, p.888]. Naphtha and gas oil plants produce an excess of fuel over and above requirements to fire the process furnace and to provide high-pressure steam for the plant’s steam-driven compressors [14, p.129].

#### Process-Side

**Run Cycle.** Hydrocarbon feed is first mixed with steam at a steam-to-hydrocarbon weight ratio which varies from about 0.3 for ethane to well over 1.0 for heavy gas oils [11, p.313; 14, pp. 91, 120; 16, p.51; 28, p.647]. The steam-hydrocarbon feed-mixture is fed through convection section of a cracking furnace, where it is heated to its incipient cracking temperature by flue gas [14, pp.122-123]. Gaseous feeds require only sensible heat. A liquid requires sensible heat to reach its vaporization temperature, plus the latent heat of vaporization [16, p.62-63]. Temperature is in the range of 500-800 °C (932-1472 °F), depending on the feedstock [9, p.886; 16, p.50]. Lower temperatures are used for heavy feeds like atmospheric gas oil (AGO) and vacuum gas oil (VGO), and higher temperatures are used for light gases like ethane and propane [9, p.886].

The hot vaporized feed then enters the furnace’s radiant section at the so-called *crossover temperature* [9, p.886] inside an assemblage of vertical alloy tubes, known as *radiant coils*. This tube assembly includes elbows and return bends connecting the vertical sections [16, pp.62-63]. Radiant pyrolysis coils are normally hung vertically from the ceiling, centered in one or two rows in a single plane between two radiating refractory walls and are fired from both sides [9, p.886; 14, p.123; 16, pp.62-63, 66]. They are usually supported on spring hangers above the top of the radiant firebox [16, pp.62-63]. In older units, the tubes were horizontal; the change to vertical tubes permitted higher throughputs [14, p.92].

The feed stream now inside the radiant coils undergoes the endothermic thermal cracking reactions, and the temperature along the coils increases as external heat continues to be added [14, p.120; 16, pp.51-52]. This energy is supplied by the fired duty of gas- and/or oil-fired burners in the radiant section of the furnace [28, p.647]. Radiant-coil outlet temperatures are maintained anywhere from 700-950 °C (1292-1742 °F) [9, p.886; 11, pp.313-314; 14, p.91; 16, pp.50, 62-63]. Temperatures are higher for ethane than for naphthas than for gas oils [16, p.50]. Tube skin temperatures can reach as high as 1950-2100 °F (1066-1149 °C) [37].

Typically, the coil outlet pressures are 172-240 kPa (25 to 35 psia) [11, p.313; 14, p.124; 16, p.51]. Residence time in the cracking zone is tenths of a second or less [9, p.886; 11, p.313; 12, p.586; 14, pp.91,120; 28, p.647].

The process effluent from the furnace, termed the *cracked gas*, must be cooled instantly in one or two stages [9, p.888] to as low as 600 °F (320 °C) [11, p.313] to stop the cracking reactions, minimize degradation of the products by undesired secondary reactions, and avoid the formation of tarry polymers and coke [9, pp.888; 11, p.314; 12, p.586; 14, p.125; 16, p.47]. The heat recovered is used to generate high-pressure steam [12, p.586] in what is termed a *transfer line exchanger (TLE)* or *quench cooler* [14, p.125]. Exit temperature from the TLE is about 300-650 °C (572-1202 °F), depending on the feedstock and the design [9, p.888; 16, pp.62-63; 83, 408].

The quenched furnace effluent then proceeds to the recovery section for separation into desired products and further purification [9, p.888; 16, p.47; 28, p.649]. The processing scheme (not shown) is much more complex for a naphtha cracker than for an ethane cracker [12, p.586].

**Decoking Cycle.** During the thermal cracking process, coking occurs inside the radiant coils and the transfer line exchangers (TLE). Periodically, the built-up coke must be removed in an offline operation whenever the tube-metal temperature and the pressure drop reach their maximum allowable limits and the ethylene yield drops [14, p.125; 16, p.68; 37]. Since mechanical techniques are not feasible [16, p.69] because of the many turns and bends in the radiant coils [16, pp.62-63], the coke is burned off in a carefully controlled process by passing a mixture of steam and air through the coils at 800-1000 °C (1472-1832 °F) [9, p.893; 12, p.284; 14, p.125; 16, p.69]. Air serves to burn off the coke, and steam keeps the combustion temperature from exceeding the maximum allowable tube-metal temperature [12, p.284]. Steam also diminishes the catalytic action of iron and nickel in the radiant-coil wall material to promote coking [16, p.51]. Transfer line exchangers are decoked in a separate procedure.

Coking can be mitigated by adding a passivating film to the inside surface of the clean radiant coils after decoking. Sulfur compounds, for example, H<sub>2</sub>S, ethyl mercaptan, dimethyl sulfide (DMS), or dimethyldisulfide (DMDS), or else proprietary phosphorous-based anti-fouling additives are used for this purpose [37; 43, Ques. 12 (Rowe)]. In addition, up to 100 ppm of sulfur compounds can also be added into the feed during the run if the feed level of "crackable sulfur" is insufficient to deplete the CO formed during coking [43, Ques. 12 (Ross, Shen); 83, p.407].

**Decoking Time and Frequency.** The amount of time necessary to decoke depends on tube-wall temperature and the relative concentrations of air and steam [16, p.69; 84]. Estimates for radiant coil decoking with steam and air range from 12 to 48 hours in general [9, p.893] to 6 to 10 hours for liquid cracking furnace and a longer time for gas cracking furnaces (ethane, propane, and butane), since these generally produce a denser coke [16, p.69].

Based on a survey presented at the 1995 A.I.Ch.E. Ethylene Producers' Conference, (32 companies with over 200 furnaces), a majority (57%) of the companies using gas feed experienced furnace run lengths between 21 and 60 days, and for liquid feed, (60%) between 21 and 40 days. In the survey, 56% of the furnaces used gas feed, while the others used gas and liquid [37]. More optimistic estimates of run times between decokings are 30 to 50 days [44], 30 to 90 days [84], 30 to 100 days [85], 45 to 60 days [86], and 40 to 100 days [9, p.891].

### Flue-Gas Side

**Combustion of Fuel in the Furnace.** At steady state, the heat absorbed by the radiant coils plus that lost through the radiant-section firebox must equal the heat given up by the flue gas as it drops from the adiabatic flame temperature to the temperature at which it leaves the firebox [16, p.67]. Firebox temperature is typically 1000-1200 °C (1832-2192 °F) [16, p.66], and the refractory walls have been measured at a uniform temperature of about 1200-1300 °C (2192-2372 °F), with only a slight drop in temperature toward the flue-gas exit end [14, p.123]. Heat is recovered by generating and superheating steam and by heating the feed, boiler feed water, or other process streams [14, pp.92, 122-123; 9, p.888] as the flue gas is cooled before being discharged to atmosphere. Temperatures of 170-200 °C (338-392 °F) immediately upstream of the stack have been reported [4]. Two cracking furnaces usually share a common stack, probably with an induced-draft (ID) fan at the base of that common stack [9, pp.886-887].

Many ethylene cracking furnaces are built with the option to use gas fuels, liquid fuels, or combinations of both, but some furnaces are all-gas or all-liquid fired [16, pp.61-66]. Fuels may be generated in the process or brought in from external sources. The by-product methane, ethane, propane, and hydrogen from the process can all be used as fuel gases in the furnace. However, the actual methane and hydrogen streams in the plant are not pure hydrogen and pure methane. The methane stream separated from the cracked gas product consists of 95% methane with some minor impurities of hydrogen, carbon monoxide, and traces of ethylene [9, p.897]. It is called *methane-rich gas* [14, pp.129] or the *pyrolysis methane fraction* [16, p.66]. The hydrogen stream separated from the pyrolysis gas product is only 85% to a maximum of 95% pure [9, 897; 14, p.132]. Some or all of it may be upgraded to higher purity for use in hydrogenation of other streams [14, p. 132]. Because further cryogenic purification of the hydrogen by-product may not be worth the additional expense [16, p.79], the impure hydrogen stream may be fired as fuel in the furnace as well. This stream is then referred to as *hydrogen-rich fuel gas* [14, pp.129; 16, p.66]. Firing a hydrogen-rich gas will increase the adiabatic flame temperature and consequently the amount of NO<sub>x</sub> generated at the furnace burners [87].

Cracking of heavier feedstocks produces appreciable quantities of liquid products. A gasoline-like liquid, high in aromatics, called *pyrolysis gasoline* is also produced [28, p.645], along with a heavier cut called *pyrolysis fuel oil*, which appears in increasingly large volumes from the heavier feedstocks [14, pp. 128-129]. Pyrolysis gasoline (pygas), a gasoline-like liquid, [12, pp.309, 689; 28, p.645] is highly unstable because of its high content of unsaturated compounds and cannot be held in storage for any length of time [14, p.128]. Only small proportions can be blended as produced into a refinery gasoline pool because of its unacceptable odor, color, and gum-forming tendency [28, p.650]. It must be hydrogenated for this purpose [12, p.309; 14, p.128; 83, p.403] or before being used as a source of aromatic chemicals [12, p.309; 83, p.403]. Pyrolysis gasoline if taken as a separate cut is unlikely to be used as a fuel in an ethylene furnace because of its potential to be upgraded for other uses.

The pyrolysis fuel oil fraction can be expected to contain the same types of components as pyrolysis gasoline plus heavier multi-ring organics as well. It is thermally unstable so that it cannot be stored for long [83, p.403]. It tends to be incompatible when blended with fuel oils from other sources [14, pp.128-129; 83, p.403]. Sulfur concentrations in the pyrolysis fuel oil in excess of environmental requirements would necessitate desulfurization of the feedstock [14, p.121]. Some furnace designs are capable of burning part pyrolysis fuel oil [4; 14, p.123; 16, p.66], and it finds a use there [83, p.403].

Natural gas, refinery fuel gas, and fuel oil of some sort are the most likely fuels to be brought in to fire an ethylene cracking furnace.

**Decoking Effluent.** The offgas from decoking contains CO, CO<sub>2</sub>, and carbon particles. [9, p.893] It is usually diverted to a decoking system containing quench water and a knockout pot [9, p.893; 16, p.69], and thence to atmosphere. Alternatively, it is combusted in a firebox [9, p.893]. This might be the ethylene furnace, or it might be some external heater with its own separate stack.

**Emissions and Emission Controls.** Stringent environmental regulations mandate that emissions of nitrogen oxides (NO<sub>x</sub>) and sulfur oxides (SO<sub>x</sub>, i.e., SO<sub>2</sub> + SO<sub>3</sub>) from furnaces be curtailed dramatically, and in many jurisdictions, NO<sub>x</sub> must be reduced to 70 ppmv or lower on a wet basis [9, p.889]. This corresponds to a dry-basis ppm some 20-25% higher [87, 88], or about 85-90 ppmvd. In the Houston-Galveston area of the Texas Gulf Coast [3] and in California, permissible outlet NO<sub>x</sub> is much less, in the single-digit ppm range in some cases. Conventional burners usually produce 100 to 120 ppmv of NO<sub>x</sub> [9, p.889]. As calculated from the factors in EPA Method 19 [89], a dry-basis NO<sub>x</sub> concentration of 100 ppmv (100 ppmvd) from natural-gas combustion at 3% O<sub>2</sub> (dry) in the flue gas is equivalent to 0.12 lb NO<sub>x</sub> per million Btu of fuel fired (lb/MM Btu), based on the higher heating value (HHV) of the fuel. The relationship is directly proportional.

Many burner manufacturers are supplying low NO<sub>x</sub> burners; however, it may not be possible to meet the strictest of standards by means of burners alone [9, p.889]. For example, John Zink has presented state-of-the-art low-NO<sub>x</sub> burner technology for ethylene furnaces in a paper delivered at 2001 A.I.Ch.E. Ethylene Producers Conference in Houston [2]. NO<sub>x</sub> was reduced to 6-12 ppmv from a single burner tested in a small furnace firing an unspecified fuel; yet, in the more practical case of a multiple-burner array in a large furnace, NO<sub>x</sub> was measured at no lower than 16 ppmv. (Reported ppm concentrations are corrected to 3% O<sub>2</sub> and are presumably on a dry basis.) This real-world reduction is substantial and more or less dramatic, depending on the fuel, but not quite good enough to meet the latest regulatory requirements. At the current state of the art, therefore, SCR will be needed to control outlet NO<sub>x</sub> at or below regulatory limits.

## APPENDIX B

### PROCESS DESCRIPTION FOR STEAM-METHANE REFORMING

#### Overview

The steam-methane reforming (SMR) process makes hydrogen by reacting steam and a hydrocarbon in the presence of a nickel-based catalyst [11 p.262; 18, pp.852, 854; 20; pp.171-172, 191; 24, p.321] (Figure, right). This catalyst, in the form of pellets, hollow cylinders, or similar shapes [11, p.262; 21; 24, p.321] is contained inside alloy tubes [18, p.854; 20, p. 179; 21; 30, Ques. 2; 31; 32; 33] suspended in the radiant section of a furnace and into which a mixture of steam and desulfurized feed is introduced. Feed is usually natural gas but can also be refinery gas, propane, liquefied petroleum gas (LPG), butane, and straight-run naphtha [18, pp. 852, 858; 21; 22].

Downstream processing (not shown) reacts additional steam to maximize the hydrogen yield, and the hydrogen product is separated from the resulting synthesis gas (syngas), a generic term for mixtures of hydrogen (H<sub>2</sub>), carbon monoxide (CO), and carbon dioxide (CO<sub>2</sub>). Hydrogen is used in petroleum refining, and hydrogen production is the first step in the manufacture of ammonia [20, p.165]. Hydrogen is also a coproduct in the manufacture of carbon monoxide (CO) [25].

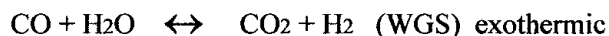
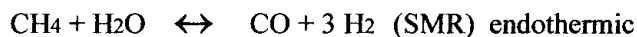
As with ethylene manufacturing, this process can also be integrated with gas-turbine exhaust [26], and the steam produced can be used instead of electric drive [24, p.326].

#### Process Side

The feed is preheated either in the furnace's convection section [24, p.327] or in a separate heater [18, pp. 855, 857] to approximately 300-400 °C (572-752 °F) [18, p.854; 19, p.951; 24, p.326]. The preheated feed must then be desulfurized because sulfur compounds act as poisons to reforming catalysts [20, p.173], reducing the activity of the catalyst and causing hot spots on the reformer tubes [18, p.858]. Reformer catalyst is typically replaced every 3 [41] to 4-5 [21] years.

In a two-step process, any organic sulfur molecules present are first hydrogenated with a stream of recycled product hydrogen over a cobalt-molybdenum catalyst at 300-400 °C (572-752 °F) [18, p.854; 24, p.326] to produce hydrogen sulfide (H<sub>2</sub>S). The H<sub>2</sub>S is then adsorbed on a bed of zinc oxide (ZnO), leaving a residual sulfur level of 0.1 ppm by weight in the feed stream [18, p.854]. The hydrogen also saturates any olefins in the feed to prevent thermal cracking and coke formation inside the furnace tubes [90, Ques.7 (Shen), 24, p.326].

Steam (H<sub>2</sub>O) is added, and the reaction mixture enters the reformer tubes inside the furnace at a maximum temperature of 1000 °F (538 °C) [21; 24, p.325], where the following reactions, shown for methane (CH<sub>4</sub>), occur, producing hydrogen (H<sub>2</sub>) and carbon oxides [20, p.192], as follows:



The endothermic [11, p.262; 20, p.165; 24, p.319] steam-methane reforming (SMR) reaction is close to equilibrium [18, p.854; 20, p.192; 21; 22; 24, p.321] at the reformer outlet temperature of up to about 1600 °F (871 °C) [18, pp.852, 854; 21]. Although typical operating pressures vary from source to source, a consensus pressure range is approximately 300-400 psig (2.17-2.86 MPa) [18, p. 852; 21; 30, Ques. 2 (Paules); 32]. This is about 10 times the pressure range for steam cracking. Space velocity (SV), the reciprocal of residence time based on an empty tube, is 5000-8000 reciprocal hours [18, p.854; 19, p.951]; actual residence time is therefore tenths of a second.

Some of the carbon monoxide (CO) reacts further with excess steam to carbon dioxide (CO<sub>2</sub>) and more hydrogen in accordance with the exothermic water-gas shift reaction (WGS) shown above [11, p.262; 24, p.319]. An excess of steam is added to prevent coke formation on the catalyst and loss of catalyst activity [20, p.167; 19, p.952]. The ratio of moles of steam to atoms of carbon in the feed is called the *steam-to-carbon (S/C) ratio* [24, p.320]. Its range of values from 2.5 to as much as 6 [18, p.854; 19, p.951; 21; 24, pp.320-321, 325] amounts to about 10 times the weight ratio of steam to hydrocarbon used in steam cracking of gaseous feedstocks [43, Ques.12 (Ross, Shen)].

At this point, the product mixture, known as *synthesis gas (syngas)*, contains percentage concentrations of hydrogen, carbon oxides (CO and CO<sub>2</sub>), excess steam, unreacted methane, and the nitrogen (N<sub>2</sub>) from a natural-gas feed, plus parts-per-million (ppm) concentrations of reaction by-products such as methanol, ethanol, and ammonia [91]. Higher hydrocarbons heavier than methane are not normally found in the syngas exiting a steam-methane reformer [24, p.321].

More steam is added [11, p.262] in one or more shift-converter vessels outside the furnace to continue the WGS reaction and produce more hydrogen (not shown in Figure 1). These vessels, are denoted as the *high temperature shift (HTS)* and *low temperature shift (LTS)* reactors and contain catalysts different from reforming catalyst and different from each other.

The remainder of the process flow sheet is concerned with separation of the hydrogen product (also not shown). When a high-purity hydrogen product (> 99.9 % H<sub>2</sub>) is required, the preferred route is pressure-swing-adsorption (PSA) [18, p.858; 24, p.328]. In this case, the syngas is cooled to ambient temperature with condensation and removal of water [24, p. 327] and as much heat recovery as possible [18, p.856]. It then enters one of several parallel vessels containing a molecular-sieve adsorbent [11, p.266, 24, p.327]. There, the impurities (anything not hydrogen) are adsorbed, allowing the small molecules of the hydrogen product to pass through [18, p.856].



Periodically, in a predetermined sequence, each adsorber vessel is taken off line for regeneration and replaced by a stand-by vessel in which the adsorbent has been regenerated [24, p.327]. Regeneration consists of dropping the pressure to release the adsorbed impurities and purging with a small stream of recycled hydrogen [18, p.856]. A surge vessel downstream dampens out fluctuations in pressure and gas composition [24, p.327].

This purge gas is used as fuel in the furnace and can provide up to 90 % of the fuel requirement for the reformer furnace burners [18, p.856]. Typical supplementary fuels are light hydrocarbons such as natural gas and refinery fuel gas, but distillate fuels are sometimes used [21]. A portion of the feed gas itself can be fired [24, p.328], and use of naphtha and heavy fuel oil as fuel has been reported [68]. However, the metals in heavy fuel oil or residual fuels can damage/corrode the reformer tubes [21, 68]. A typical purge-gas composition with make-up natural gas can be found in References [87] and [88].

An older version of the separation process involves scrubbing with a regenerable amine solution or hot potassium carbonate [11, p.262; 19, p.952; 18, p.856; 24, p.328] or another solution [19, p.952; 18, p.856] to remove CO<sub>2</sub>. This is followed by methanation [11, p.262; 18, p.856; 19, p.952; 24, p.328], a reversal of the SMR reaction, to remove the unreacted methane. This method produces a hydrogen purity of 90-98 % [91], results in a large by-product CO<sub>2</sub> stream, and requires an external fuel, as described above, to fire the furnace.

**Flue-Gas Side.** Combustion of fuel provides the necessary radiant heat to drive the endothermic reforming reaction. The temperature at which the flue gas exits the radiant firebox, referred to as the *bridgwall temperature* [24, p.322], is stated as 1800-1900 °F (approx. 980-1040 °C) [18, p.854; 21], although one source quotes a higher upper end, 2200 °F (ca. 1200 °C) [32]. Heat from the flue gas is recovered in the convection section by such means as preheating the feed, producing/superheating steam, and perhaps preheating the combustion air [18, p.854; 19, p.951; 24, p.325]. Temperature at the stack following waste heat recovery is said to be about 300 °F (~150 °C) [21], 200-260 °C (392-500 °F) [19, p.951], and 150-170 °C (302-338 °F) [18, p.854], depending on the type and amount of heat exchange with other fluids. Large furnaces are typically equipped with both a forced draft (FD) and an induced-draft (ID) fan [24, p.325] and operated at a slight negative pressure (a few millimeters of watergauge below ambient pressure) [20, p.178].

**Emissions and Emission Controls.** Combustion of a fossil fuel generates nitrogen oxides (NO<sub>x</sub>) here as well. Depending on the type of burners, air preheat, and fuel, NO<sub>x</sub> concentrations up to 100 ppmv or more have been reported [22, 87, 88]. Firing a PSA purge-gas mixture can give lower emissions, e.g., 0.03 lb NO<sub>x</sub>/MM Btu based on the lower heating value (LHV) [21]. This is equivalent to about 25 ppmv (dry) at 3 % O<sub>2</sub> (dry) [87, 88]. Selective catalytic reduction (SCR) can be applied, as necessary, to reduce NO<sub>x</sub> emissions still further [20, p.184; 22]. Sulfur-oxide emissions from burning PSA purge gas will be lower because of the feed-desulfurization step. Some current regulatory limits for NO<sub>x</sub>, CO, and particulates are listed in Ref. [92].

## APPENDIX C

### ALLOYS USED FOR FURNACE COILS/TUBES

There is considerable overlap between the alloys used to manufacture ethylene pyrolysis coils and the catalyst-filled tubes suspended in the furnace of a steam-methane reformer (SMR) hydrogen plant. Nominal compositions compiled from several sources are shown in Table 3 of the main text. The alloys are commonly referred to either by their American Iron and Steel Institute (AISI) or Alloy Casting Institute (ACI) designations such as Type 304 or HK-40, by their percentages of chromium and nickel, e.g., 25Cr/35Ni, or by their trade names like 36X or Supertherm. The same alloy be known in the industry by more than one name.

These alloys consist of chromium and nickel with smaller amounts of carbon, silicon, manganese, and some other ingredients. Chromium imparts a stable oxide film to protect the tube's/coil's combustion (outside) and process (inside) surfaces from further oxidation,<sup>37</sup> but it introduces instability in the alloy structure unless counterbalanced by adding nickel and other elements.<sup>36</sup> Silicon (Si) also promotes oxidation resistance.<sup>36</sup> Chromium, nickel, and silicon inhibit carburization, the penetration of carbon from contact with hydrocarbon gases or coke into the alloys to weaken the alloy structures.<sup>36</sup> Other ingredients enhance performance in various ways.<sup>36</sup>

In 1984, an industry consultant enumerated the principal alloys employed for ethylene and SMR applications, along with the different trade names assigned to those alloys by a number of suppliers;<sup>46</sup> alloy compositions were listed in a subsequent article.<sup>80</sup> This analysis was updated within the past six years for each process separately by that same consultant.<sup>36,38,39</sup>

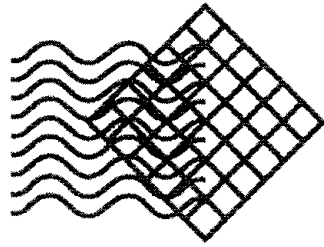
The first ethylene units in the 1950s used AISI Type 304 stainless steel. As the furnaces became larger and temperatures increased, Type 316 stainless steel and Incoloy Alloy 800 came into use for pyrolysis coils. These were followed by ACI HK-40, which was to become the standard, most widely used alloy for many years.<sup>36,37,44,80</sup> The choices for SMR catalyst tubes followed a parallel course,<sup>31,38,39,46,80</sup> although some SMR furnaces used the International Nickel Company (INCO) Alloy IN 519.<sup>46</sup>

As operating temperatures continued to rise beyond the limitations of HK-40, the HP-type alloys (including, for example, HP-40, HP-45, and HP-50) were introduced for both services.<sup>20,36,38,38,45</sup> A broad range of modifications of the HP alloys have now been prepared by adding combinations of niobium (Nb) (once called columbium (Cb)), tungsten (W), and molybdenum (Mo)). No two of these alloys are exactly alike, but their differences are not judged to be significant.<sup>38,38</sup> Many are considered proprietary<sup>38,39,46</sup> but are offered with minor changes by other manufacturers.<sup>38,39</sup>

Of these modifications, HP + ~1-1.5% Nb is the most common variation, with "microalloys" containing trace quantities of titanium (Ti), zirconium (Zr), and rare earths in addition to the Nb seeing greater usage. Specialty alloys like 35Cr/45Ni permit even greater tube-metal temperatures beyond those achievable with the original HK-40 standard or the HP Mods.<sup>37-39</sup> Tube-metal temperatures may vary from 1750 °F to as high as the 1950-2100 °F range for ethylene plants<sup>36,37,43,44-46</sup> and somewhat lower in the 1600 °F to 1925 °F range for hydrogen reformers.<sup>21,24,32,41,46</sup>

The ethylene industry has now standardized more or less on HP Mod materials for pyrolysis furnaces.<sup>36</sup> The HP Mod Nb alloy has been adopted as a standard for steam-methane reformers as well.<sup>32</sup> The ammonia industry has used HP Mod alloys in the hydrogen plant primary reformer since the 1980s;<sup>38,39</sup> this is consistent with hydrogen-plant literature<sup>21,22</sup> and a spot sampling of hydrogen plant designers and operators.<sup>30</sup> Some IN 519 and HK-40 tubes may nonetheless still remain in steam-reforming service in older plants.<sup>20,40,41</sup> Tube/coil life is designed for 100,000 hours (11.4 years)<sup>22,30,33,36,41</sup> or more,<sup>30</sup> prematurely shortened<sup>30,31,43,45,46,80</sup> by overheating,<sup>31,38,39,46,80,82</sup> other thermal stresses,<sup>33,38,39,80</sup> and carburization.<sup>37,45,80,93</sup>

One is therefore led to conclude that both ethylene plants and steam-methane reformers at the present time employ tube-metal alloys of a very similar composition containing upwards of about 25% chromium.



CORMETECH

# **SCR Treatment of** **Ethylene Furnace** **Flue Gas**

## **(A Steam-Methane Reformer in Disguise)**

Presented by

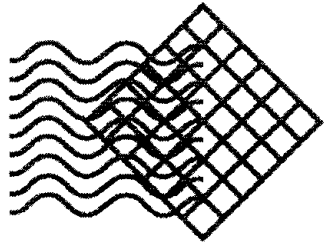
**ROBERT G. KUNZ, Ph.D, P.E.**

**&**

**T. Robert von Alten**

**ICAC Forum 2002**

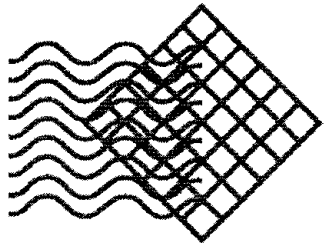
**February 12-13, 2002**



CORMETECH

# Overview

- Terminology
- Comparison of Processes
- SCR Reactions
- Reported SCR Experience
- Chromium Deposition
  - ❖ Oxide Scale
  - ❖ Vaporization
  - ❖ Mass Transfer
- Conclusions



CORMETECH

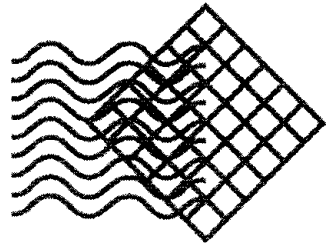
# Terminology

## ➤ Ethylene

- ❖ Process: Cracking, Thermal Cracking, Steam Cracking, Pyrolysis
- ❖ Equipment: Steam Cracker, Ethylene Furnace, Pyrolysis Furnace, Ethylene Plant

## ➤ Hydrogen

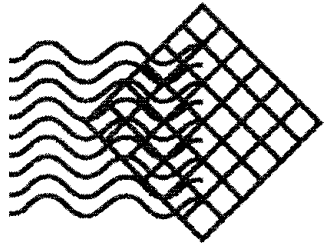
- ❖ Process: Steam Reforming, Methane Reforming, Steam-Methane Reforming
- ❖ Equipment: Steam Reformer, Steam-Methane Reformer (SMR), Primary Reformer, Hydrogen Plant



CORMETECH

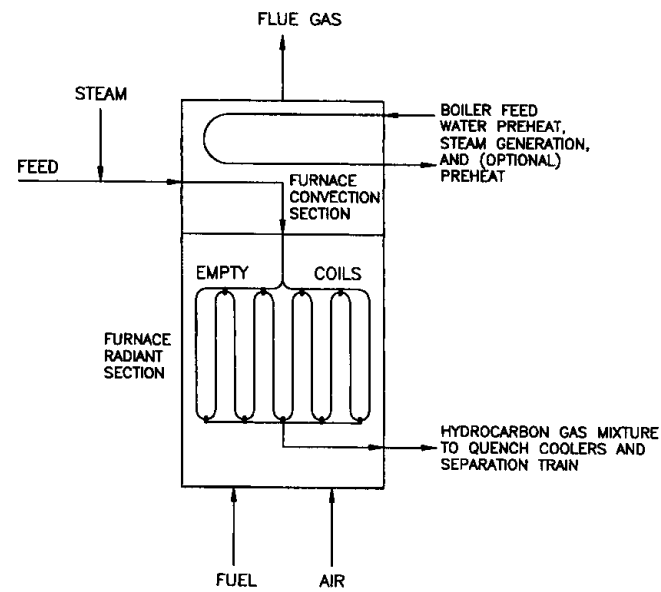
# Two Processes Compared

- **Ethylene Production by Steam Cracking**
- **Hydrogen Manufacture by Steam- Methane Reforming**

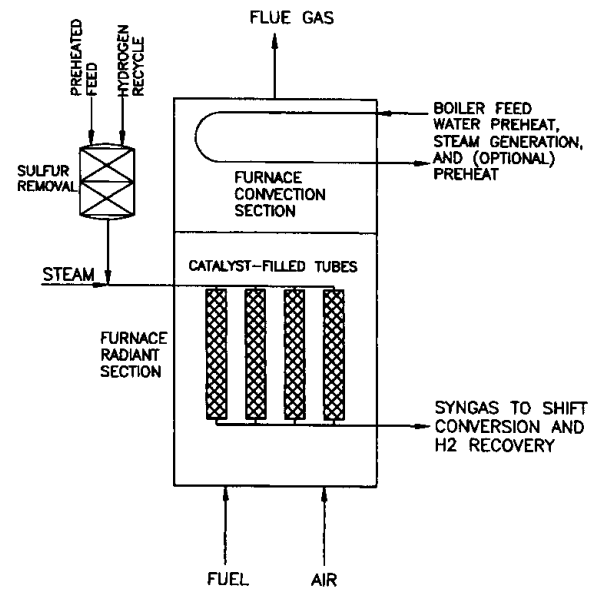


CORMETECH

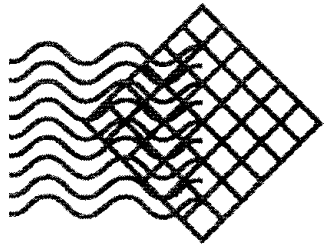
ETHYLENE PYROLYSIS FURNACE



STEAM-METHANE REFORMER FURNACE



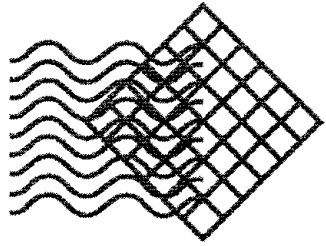




CORMETECH

# Processes Are Different, But Furnaces Are Similar

- Uniform Heat Distribution via Many Small Burners
- Same Imported Fuels
- Air or Gas-Turbine Exhaust
- Same Alloys for Coils / Tubes
- Similar Temperatures
- Chromium Vaporization



CORMETECH

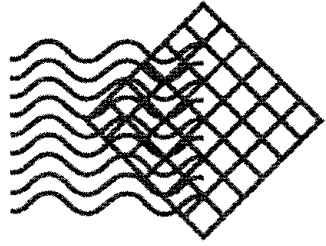
# Internally Generated Fuels

## ➤ Ethylene Plant:

- ❖ Methane-Rich Gas
- ❖ Hydrogen-Rich Gas
- ❖ Ethane / Propane
- ❖ Pyrolysis Fuel Oil

## ➤ Hydrogen Plant:

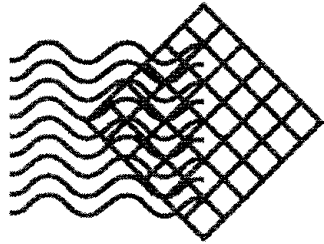
- ❖ PSA Purge Gas
- ❖ Feed Gas (Possibly)



CORMETECH

# Imported Fuels for Either Process

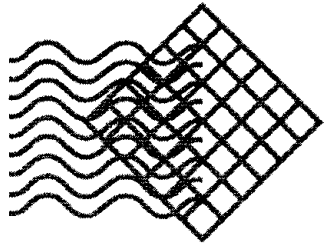
- Natural Gas
- Refinery Fuel Gas
- Distillate Fuel Oil



CORMETECH

# Furnace Coils / Tubes Contain Approximately 25% Cr

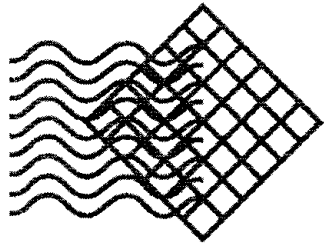
- In Current Use:
  - ❖ HP-Type Alloys, Modified with Niobium (Nb),  
“Microalloyed”
- Previously Used:
  - ❖ HK-40, IN 519 (SMR Tubes)
- Historical:
  - ❖ Incoloy 800; 304, 310 SS



CORMETECH

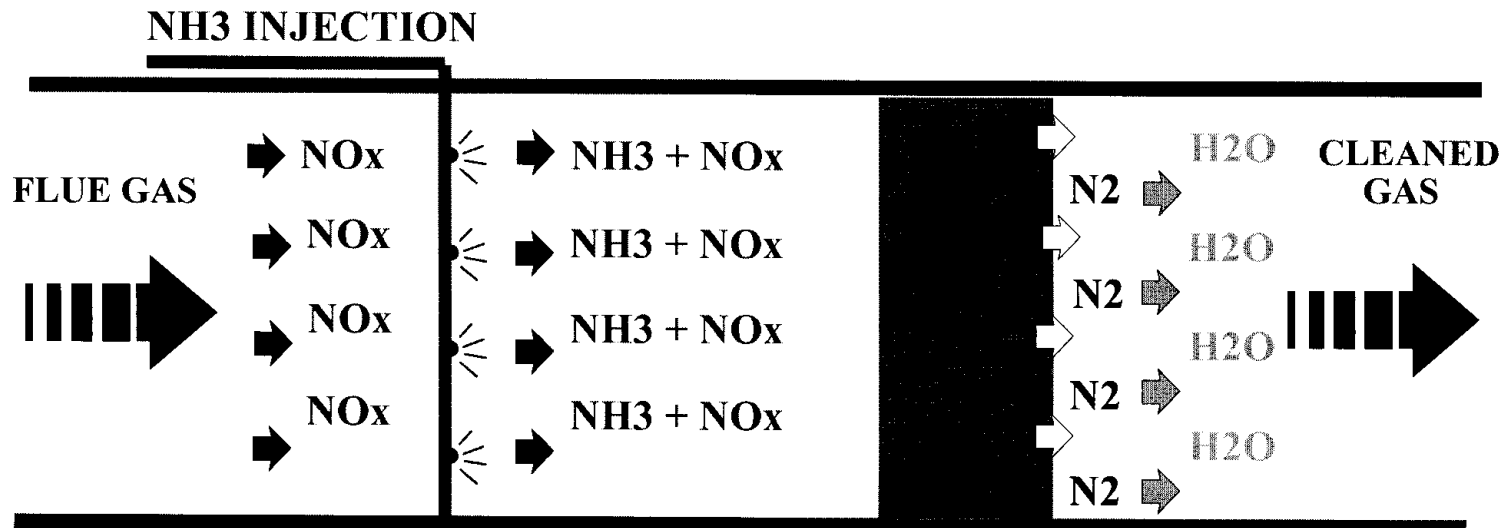
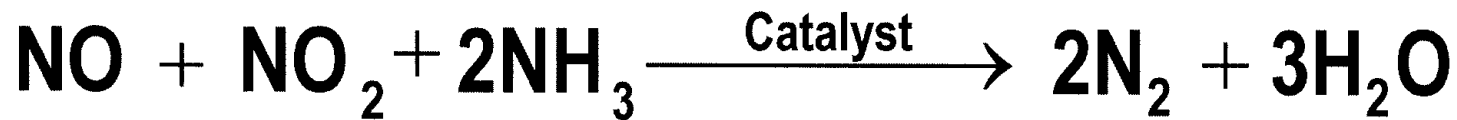
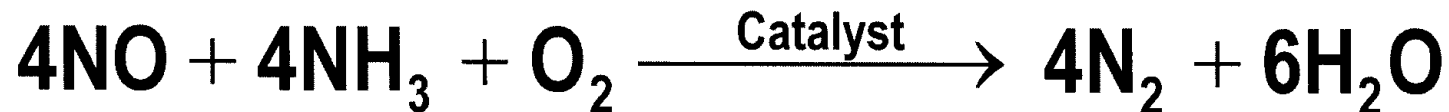
# Approximate Temperatures (°F)

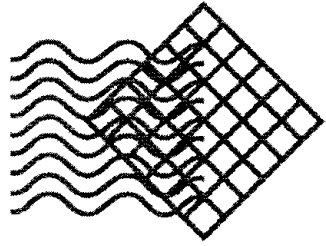
<b><u>Process</u></b>	<b><u>Furnace</u></b>	<b><u>Tube - Metal</u></b>
Ethylene	1830 – 2200	1750 – 2100
Hydrogen	1800-1900 Up to 2200	1600-1925



CORMETECH

# SCR Reaction Chemistry

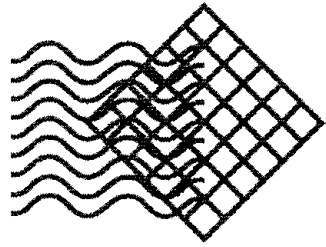




CORMETECH

# Reported SCR Experience

- Ethylene Plants:
  - ❖ Maruzen (Ichihara, Japan)
  - ❖ Idemitsu (Chiba, Japan)
- Hydrogen Plant:
  - ❖ Air Products and Chemicals, Inc.  
(Martinez, CA, USA)



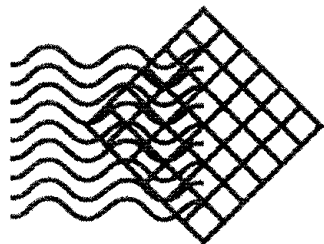
CORMETECH

# Synopsis of Experience

The Martinez SMR Plant showed greater  $\text{NO}_x$  removal efficiency and achieved a lower outlet  $\text{NO}_x$  concentration.

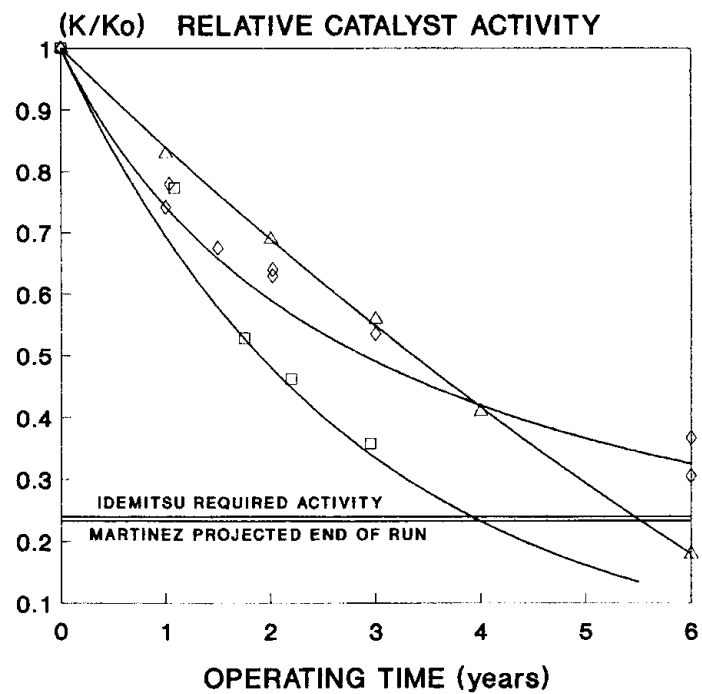
All three plants showed SCR Catalyst contamination by Cr species.





CORMETECH

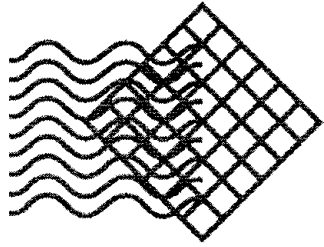
### DECLINE IN SCR CATALYST ACTIVITY DATA AND CURVES FROM LITERATURE SOURCES



□ MARTINEZ H<sub>2</sub> DATA      ◇ MARUZEN C<sub>2</sub>H<sub>4</sub> DATA  
△ IDEMITSU C<sub>2</sub>H<sub>4</sub> DATA      — CURVES AS DRAWN

IDEMITSU REQUIRED ACTIVITY

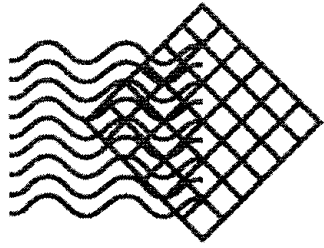
MARTINEZ PROJECTED END OF RUN



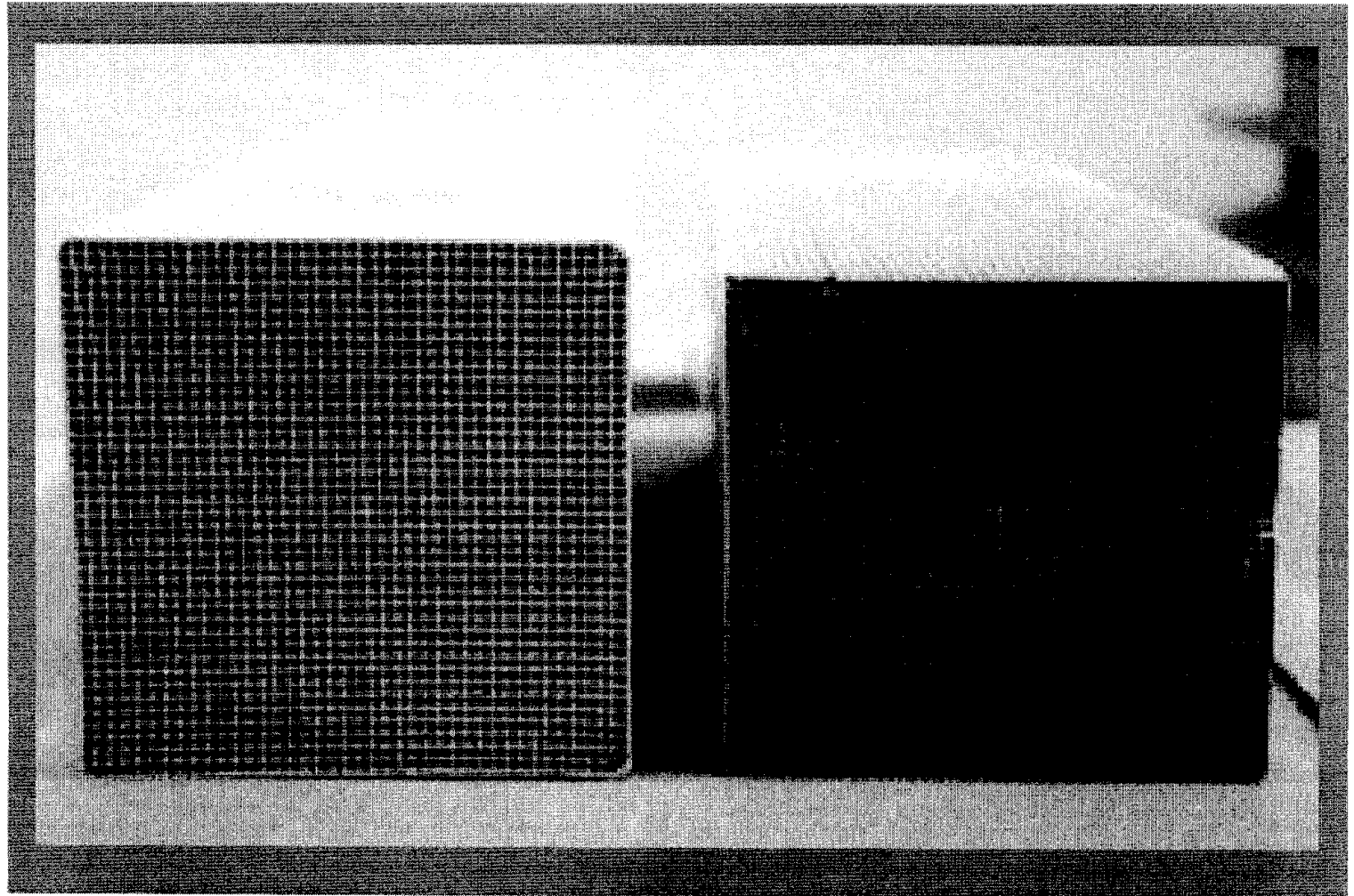
CORMETECH

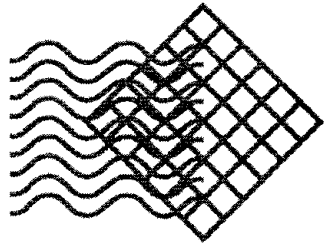
# Cause of Activity Loss

SCR Catalyst activity decays because of pickup of Cr species from the metallurgy in contact with hot flue gas, thus masking active catalyst sites.



CORMETECH

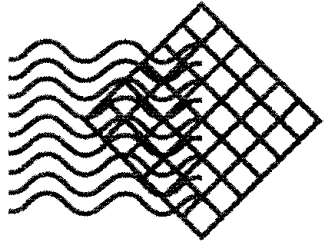




CORMETECH

## Must Investigate Upstream Conditions for the Cause

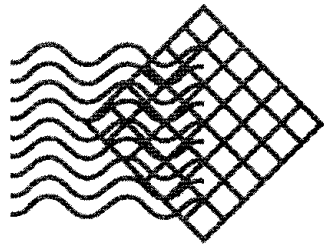
- Transport of  $\text{Cr}_2\text{O}_3$  Depends upon:
  - ❖ Formation of Oxide Scale
  - ❖ Vaporization into Flue Gas
  - ❖ Then, Capture by SCR Catalyst



CORMETECH

# Composition of Oxide Scale

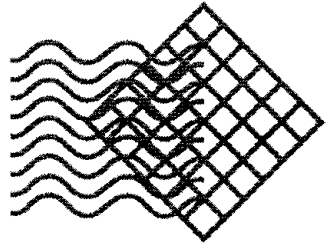
- Multiple Layers – Spinel,  
 $\text{Cr}_2\text{O}_3$ , perhaps  $\text{SiO}_2$
- Vapor enriched in Chromium
- Metal Surface Deficient in Cr



CORMETECH

# $\text{Cr}_2\text{O}_3$ Undergoes Oxidative Vaporization at High Temperature

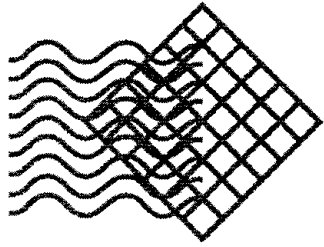
- $\text{Cr}_2\text{O}_3$  Vaporizes and Disproportionates
- Product Species Revert to  $\text{Cr}_2\text{O}_3$  upon Condensation
- With Excess  $\text{O}_2$  present,
  - ❖ Product Mix Changes
  - ❖  $\text{Cr}_2\text{O}_3$  Forms as well
- With  $\text{O}_2$  &  $\text{H}_2\text{O}$ , Gaseous Hydroxides and Oxyhydroxides Form
- “Vapor Pressure”
  - ❖ Sum of Partial Pressures of Individual Species
  - ❖ Varies with  $\text{O}_2$  &  $\text{H}_2\text{O}$  by Orders of Magnitude
  - ❖ Temperature Dependence, However, Much more moderate



CORMETECH

# Mass Transfer of $\text{Cr}_2\text{O}_3$ Depends Upon

- Flue Gas  $\text{O}_2$  and  $\text{H}_2\text{O}$
- Temperature
- Composition of Oxide Scale and Metal Surface
- Diffusion within:
  - ❖ Metal and Scale
  - ❖ Fluid-flow Boundary Layer
  - ❖ Flue Gas Velocity



CORMETECH

# Conclusions

- SCR will be used to comply with most stringent NO<sub>x</sub> regulations
- SCR Catalyst performance degraded by Chromium species in:
  - ❖ Ethylene Plants
  - ❖ Steam-Methane Reformers (SMRs)
- Prediction from first principles difficult, at best
- Can rely on body of data from SMR Plants
- More information to follow