

# A kinetic model for TGU Hydrogenation Reactors - What temperature profiles say about catalyst aging and poisoning

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## Introduction

A vital contribution to quality of life on this planet has been achieved through reducing atmospheric sulfur emissions from fuel, refining processes, sulfur recovery units and other industrial processes. Significant abatement to sulfur emissions in the refining and gas processing industry was addressing the Claus sulfur recovery unit (SRU) performance with addition of tail gas units (TGU). These units reduce sulfur emissions and improve air quality, helping realize air quality/environmental goals established with the 1970's Clean Air Act and European Environmental Action Programme 1973. The most widely applied TGU is the SCOT-type with hydrogenation reactor for reduction of all sulfur species to  $H_2S$  and subsequent recovery and recycle of  $H_2S$  to the Claus front end thermal reactor. World Bank standards now require TGU level of performance for all but the smallest SRU's.

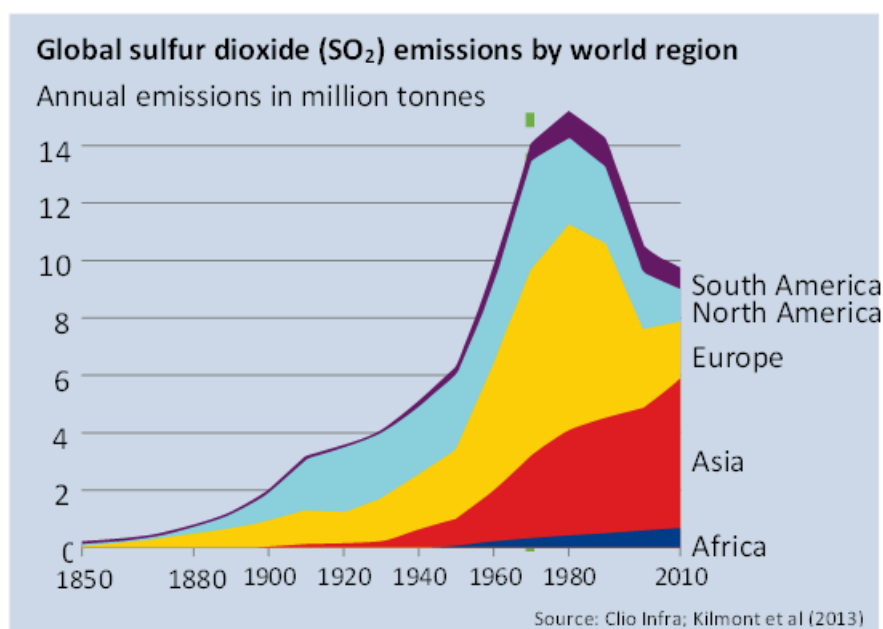


Figure 1 - Global sulfur dioxide emissions

Across the 50+ years of TGU application many improvements have been realized, increasing process efficiency, raising sulfur recovery and reducing capital cost. Contributions include more effective process design, improved catalyst performance, enhanced solvent selectivity, as well as development of sophisticated process simulation tools.

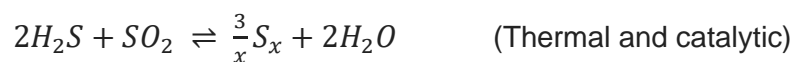
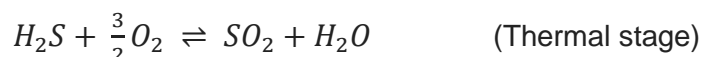
A recently developed rigorous model for reaction kinetics and catalyst deactivation mechanisms capable of predicting SRU and TGU performance is discussed in this paper. This work identified molecular reaction pathways and reaction rates for chemical species that are encountered in tail gas hydrogenation reactors as function of temperature and residence time. The resulting model was implemented as a fixed bed hydrogenation reactor in OGT SulphurPro®, a rate-based process simulator widely used in the modeling of Sulphur Recovery and Tail Gas Treating Units.

Engineering analysis needs to assure environmental performance standards are achieved for initial or start-of-run conditions as well as throughout life to end-of-run. Quantifying performance expectation across time is also necessary. Catalysts decline in activity, aging as they are exposed to process conditions and are poisoned by process contaminants. It is now recognized that since catalyst activity declines that provision must be made to include sufficient catalyst (or operational flexibility) to achieve environmental performance at end-of-run, at which time catalyst can be replaced. The model developed in this work provides a means to address the aging and poisoning effects, which in turn will help engineers optimize design, forecast operations, review performance and troubleshoot using the analysis of operating data against model predictions.

## Process Background

The sulfur recovery complex in a refinery or gas plant is visualized as a part of the overall system for extraction of H<sub>2</sub>S, other acid gases and organic sulfur compounds from the process. The acid gas removal system is regenerated and produces an acid gas (and often sour water gas) which is processed in the sulfur recovery unit (SRU), comprised of Claus, TGU, and Thermal Oxidizer. Sulfur compounds are recovered as elemental sulfur or emitted to the atmosphere.

Fundamental Claus process chemistry converts H<sub>2</sub>S to sulfur in two to three stages with about 95-97% recovery efficiency:



The tail gas unit processes off-gas from the Claus unit and achieves the very high sulfur recovery required by today's environmental standards. Although an independent process, a TGU is an integral part of the SRU. Process chemistry involves the catalytic conversion of non-H<sub>2</sub>S sulfur species to H<sub>2</sub>S, continuation of Claus, and conversion of carbon monoxide to hydrogen. Hydrogen aids hydrogenation reactions in addition to reducing CO emissions. Summary of the reactions of various sulfur species in the catalyst bed is given below:

- COS, CS<sub>2</sub>                      - hydrolysis on alumina
- SO<sub>2</sub>, S<sub>x</sub>, COS, CS<sub>2</sub>        - hydrogenation on Co/Mo
- CO                                - water gas shift on Co/Mo

The process chemistry is more complex, with several parallel reactions as well as reactions between  $\text{SO}_2$  and other reduced sulfur species. A more comprehensive discussion of reaction pathways is presented in the model development section.

The overall TGU process is depicted in Figure 2. The process gas is preheated and charged to the hydrogenation reactor for conversion of sulfur compounds to  $\text{H}_2\text{S}$  over cobalt-molybdenum catalyst. After quenching to remove water, recovery of  $\text{H}_2\text{S}$  is accomplished with a selective amine while the off-gas is incinerated and vented to atmosphere. Amine regeneration recycles  $\text{H}_2\text{S}$  to the SRU reaction furnace. A high degree of sulfur recovery is achieved by substantial conversion of all species to  $\text{H}_2\text{S}$ . The TGU obtains low sulfur slip with overall SRU/TGU recovery performance of 99.9% or better.

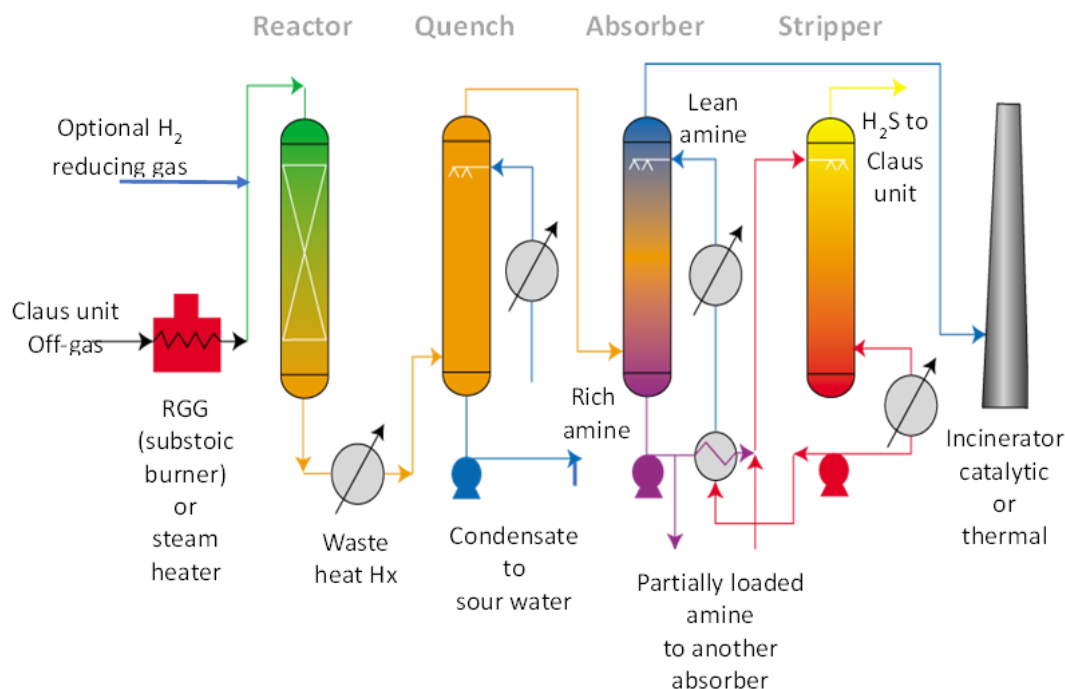


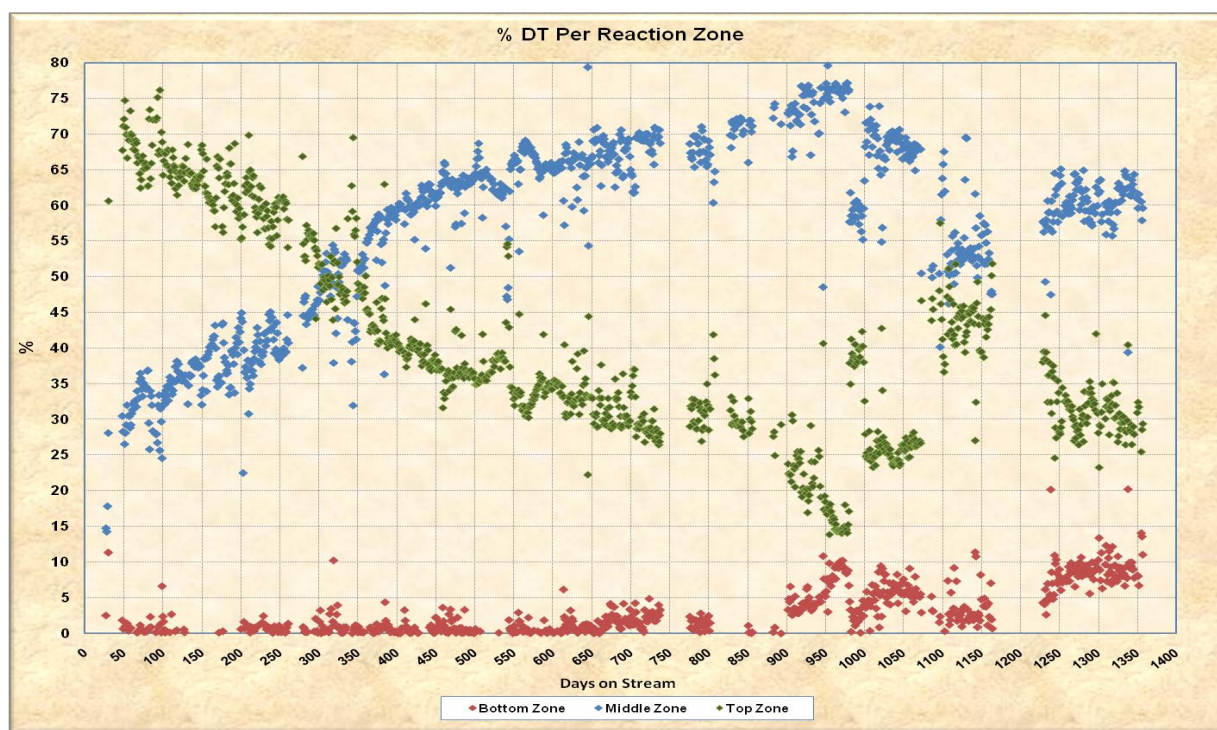
Figure 2 - Tail Gas Treating Unit

Critical performance features for TGU catalysts are foremost that  $\text{SO}_2$  should be fully converted, lest residual  $\text{SO}_2$  enter the quench circuit, foul, corrode, and potentially deactivate and subsequently degrade the amine. A high degree of conversion is required for COS,  $\text{CS}_2$  and mercaptan, as these components pass through the amine system on to incineration and are discharged to atmosphere as  $\text{SO}_2$ . Finally, the elemental sulfur must be converted or the quench circuit will plug and corrode.

Design of a TGU, historically, is carried out with an expectation of a hydrogenation reactor loaded with fresh catalyst. The reactor designer selects temperature and catalyst quantity necessary to achieve high conversion of non- $\text{H}_2\text{S}$  sulfur compounds and thus meet environmental performance requirements. The importance of compliance with permitted environmental emissions from start-of-run to end-of-run means sufficient catalyst inventory must be provided such that even in an aged condition, the required sulfur recovery performance is achieved.

A temperature profile of TGU reactor is commonly used to provide insight on catalyst performance and health. Presented in Figure 3 is the operating data for a typical refinery TGU showing temperature profile across a four-year operating window.[1] The adiabatic reactor experiences temperature rise from the exothermic reactions associated with conversion of various sulfur species to  $H_2S$  and shift of carbon monoxide to hydrogen. Three approximately equal segments of the bed are shown with their percentage of overall temperature rise across the bed: top zone is green and shows 70% of DT, middle zone is blue with 30% DT, and bottom zone is red with negligible DT. The fresh catalyst is achieving almost complete conversion in the first two zones.

Overall temperature rise across the bed is virtually constant across time (although not shown), reflecting that even with sulfur slip as outlet concentrations of non- $H_2S$  species increase, there is still high percentage conversion. The magnitude of temperature rise is related primarily to the concentration of sulfur dioxide, carbon monoxide, and elemental sulfur in the feed. The relative amount of temperature rise in each zone reflects degree of conversion in each zone.



*Figure 3 - Temperature profile operating data of a typical refinery over days*

Distribution of temperature rise between top and middle zones is dependent on overall gas hourly space velocity and catalyst activity. Temperature rise shifts between zones as bed activity declines across time. Initially, top and middle zones show temperature rise. Mid-life activity distribution shifts to 20% rise in top, 70% in middle zone, and 5% in bottom, eventually moving lower in the middle and more into the bottom zone as the top and middle zones become less active. An overall deactivation of catalyst is reflected as well as more significant activity loss in the upper portion of the bed, closer to the inlet.

Temperature profile chart indicates activity decline, which would be due to catalyst deactivation by aging and poisoning. The significance of reactor bed temperature profile shift and implication about aging, poisoning and potential bed life and the new modeling tool is the topic of this paper.

## Reaction Kinetics Framework and Model Development

Traditional perspective of TGU reaction matrix is hydrolysis on alumina along with hydrogenation and water gas shift on CoS/MoS<sub>2</sub>. To this basic frame, an expanded equation set is provided to quantify the multiple pathways involving SO<sub>2</sub>, also Co/Mo catalyzed. These reactions are parallel to the conventional address compositional dependent observations. Whereas stoichiometry for the reaction is well known, reaction order and kinetics must be determined from reaction rate data and generally these do not follow stoichiometric coefficients.

Reactant(s)	Products			
	Reverse	Hydrolysis	Hydrogenation	Shift / Exchange
<b>COS</b>	X	H <sub>2</sub> S + CO <sub>2</sub>	--	H <sub>2</sub> S + CO
<b>CS<sub>2</sub></b>		H <sub>2</sub> S + COS	H <sub>2</sub> S + CH <sub>3</sub> SH	--
<b>SO<sub>2</sub></b>		--	H <sub>2</sub> O + S (or H <sub>2</sub> S)	
<b>S</b>		--	H <sub>2</sub> S	
<b>CO</b>	X	--	--	H <sub>2</sub> + CO <sub>2</sub>
<b>CH<sub>3</sub>SH</b>			H <sub>2</sub> S + CH <sub>4</sub>	
<b>SO<sub>2</sub> + CS<sub>2</sub></b>				CO <sub>2</sub> + S
<b>SO<sub>2</sub> + CO</b>				CO <sub>2</sub> + S
<b>Claus H<sub>2</sub>S+SO<sub>2</sub></b>				S + H <sub>2</sub> O

The following steps were carried out in the development of the reaction kinetics model:

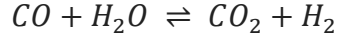
1. Collection of published experimental data
2. Postulation of a reaction set
3. Determination of reaction order from published data
4. Assessment of equilibrium influences, if > 10% outlet, include reverse reaction
5. Determination of kinetic rate temperature coefficients for Arrhenius expression from data
6. Identification and regression of compositional resistances to reaction rates
7. Refinement of the reaction set and rates with experimental and operational observations

The kinetic rate model was fitted against experimental data published in 2013 and 2016 at Brimstone. [1, 2] An apparent kinetics approach was adopted in this work which lumps the intrinsic site-based kinetics,  $k_{int}$  with effectiveness factor,  $\eta$ , for resistances to reaction rate that arises from mass transfer and diffusional effects in the catalyst pellet.

$$k_{app} = \eta * k_{int} \quad \text{and} \quad k_{app} = A * e^{-E_a/RT} \quad (\text{Arrhenius})$$

This decision was based on consideration of magnitude of Thiele modulus and effectiveness factors. Experimentally determined effectiveness factors were 0.7 or greater, although this excludes sulfur dioxide and elemental sulfur reactions. These reactions are generally first or second order, so there is concern of confounding kinetics if mass transfer presents controlling resistance. The approach provided good representation of temperature dependent kinetics using Arrhenius based rate coefficients determined from the experimental data. Operational domain for fluid dynamics in commercial applications has sufficient velocity that stagnation/back flow areas are not significant influence on bed fluid dynamics/ reactor efficiency.

The effect of adsorption resistances and compositional interaction with the reaction rate were modeled using either Langmuir-Hinshelwood type factors or fractional order rate expression. An example of this application can be seen in CO shift kinetics analysis interaction with hydrogen and water and carbon dioxide.



Water is usually present in substantial excess (normally this reaction kinetics would be addressed as pseudo first order with water as zero order) but competitive adsorption of water on active sites influences reaction rate. Additionally at lower concentrations of water reaction rate declines, exhibiting second order behavior. The Langmuir/Hinshelwood relationship provides an effective form to represent this relationship.

$$rate = \frac{-[CO] * k_{eff} * K_b * [H_2O]}{(1 + K_w[H_2O]^{aw} + K_c[CO_2]^{ac} + K_h[H_2]^{ah})^d}$$

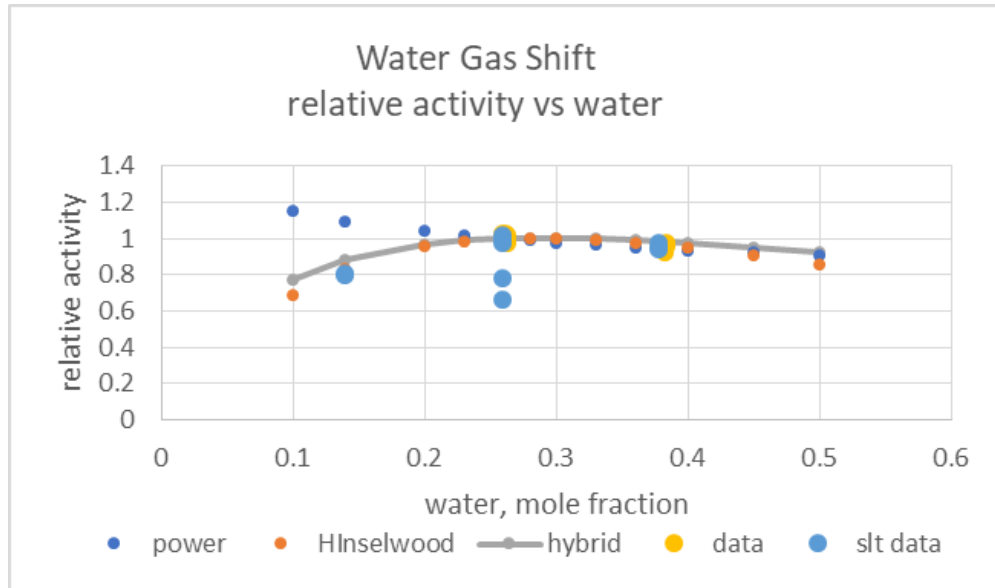


Figure 4 - Water Gas Shift reaction – Resistance from water

Hydrogen is a product of the reaction yet it has an influence beyond an equilibrium limitation expression because it is strongly adsorbed and as a leaving group it becomes rate limiting, restricting access to new reactants. The impact of hydrogen can be represented as a fractional order compositional dependency or with the adsorption mechanism.

$$rate = -k_{eff}[CO][H_2]^a[H_2O]^b[CO_2]^c$$



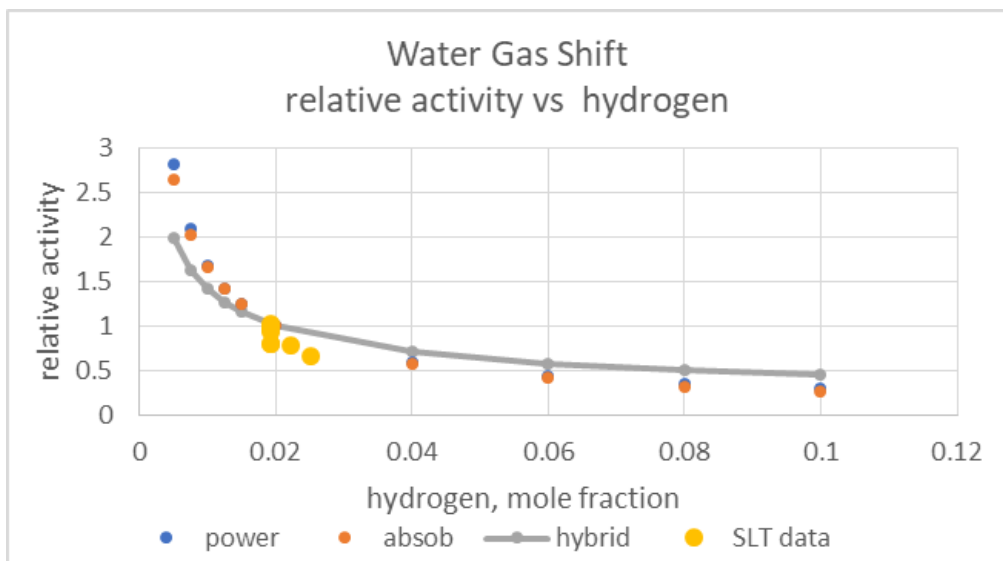


Figure 5 - Water Gas Shift reaction – Resistance from hydrogen

The hydrolysis reaction of COS is reversible and equilibrium limited as are the shift reactions of CO and COS. All the other reactions have diminishingly small equilibrium values and are considered irreversible. When reversible, kinetics must respect equilibrium so forward and reverse comply with:

$$k_{\text{forward}}/k_{\text{reverse}} = K_p \text{ and } k_{\text{reverse}} = k_{\text{forward}}/K_p. \text{ where } K_p = [R]^r [S]^s / ([A]^a [B]^b)$$

The hydrolysis reaction of COS and shift reactions of CO and COS share several components so these are reaction pathways in parallel. Since the reaction system is not at equilibrium kinetic parameters for all paths need to be defined, including reverse reactions. Additionally COS is a product of CS<sub>2</sub> hydrolysis.

An interesting aspect of CS<sub>2</sub> hydrogenation is formation of methyl mercaptan which is then further hydrogenated to methane and hydrogen sulfide. The first reaction extent, production of methyl mercaptan, is determined as the sum of mercaptan and methane, which then allows fitting for conversion or mercaptan to methane.

SO<sub>2</sub> has multiple roles in TGU reaction kinetics. A known effect of SO<sub>2</sub> is the moderation of hydrolysis of COS and CS<sub>2</sub> [3]. The more subtle role of SO<sub>2</sub>, revealed with discretized finite element bed modeling, is providing an alternate conversion pathway for CS<sub>2</sub>, moderating production of mercaptan and COS. Additionally, SO<sub>2</sub> provides a direct conversion of CO (vs. water gas shift/hydrogenation) acknowledging a substantial enhancement influence on CO conversion when present.

Parity plots comparing the outlet concentrations measured from experimental runs against the model predictions are provided for CO, COS and mercaptan and methane in Figure 6.

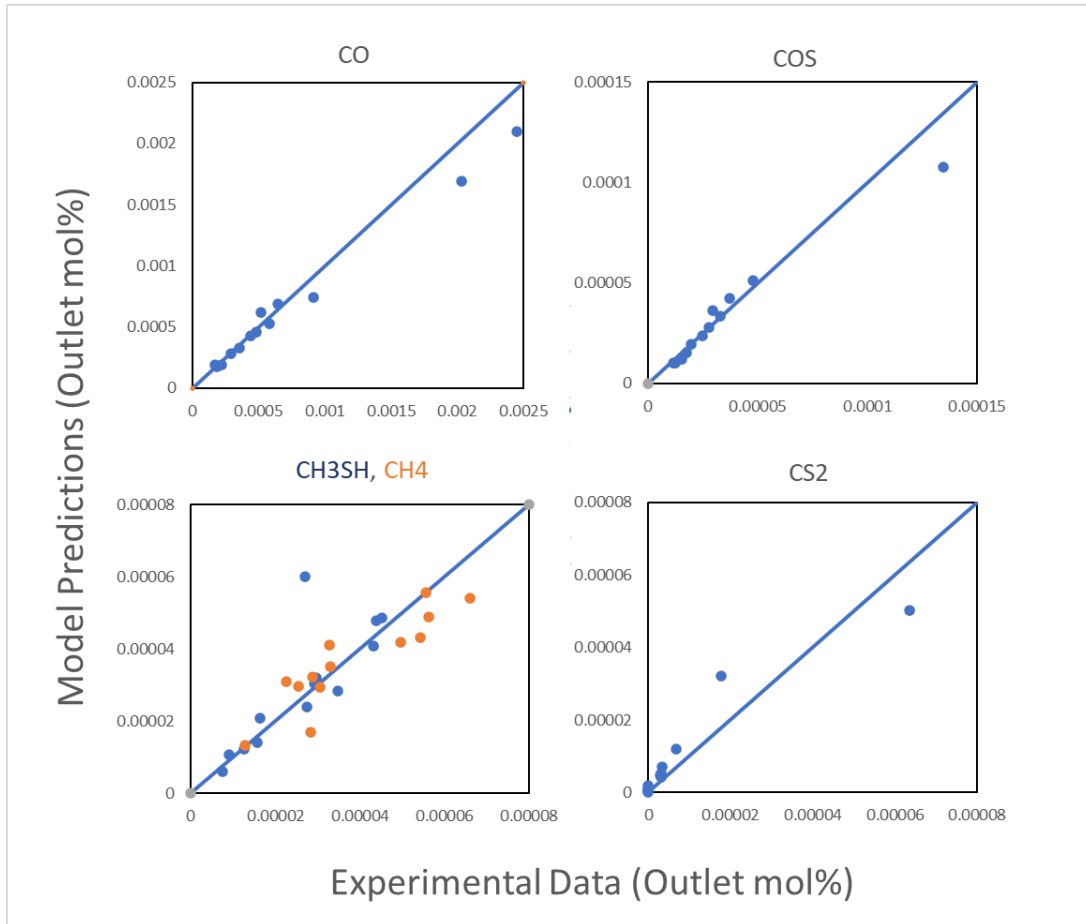


Figure 6 - Parity plots comparing outlet gas concentration from experimental data to model predictions

The parity plots show good fit of data across operation range of temperature from 260 °C to 335 °C and actual gas hourly space velocity from 1,500 to 6,000 hr<sup>-1</sup>. Composition of the feed was:

H<sub>2</sub> = 2%; CO<sub>2</sub> = 7%, 14%, 21%; H<sub>2</sub>S = 0.8%; CO = 1%; COS = 0.025%, 0.05%; SO<sub>2</sub> = 0.4%, 0.2%, 0%; CS<sub>2</sub> = 0%, 0.025%; H<sub>2</sub>O = 13%, 26%, 39%; N<sub>2</sub> = balance.

This rigorous reaction kinetics model was ultimately implemented as a hydrogenation reactor model in SulphurPro thus providing an essential cog in rate-based, plant-wide simulation of SRUs and TGUs. The reaction scheme composed of 11 individual reactions. The reactor is represented by a series of small discrete segments. In each segment the progress of each reaction is represented as:

$$\Delta C_a / \Delta x = -C_a^n * C_b^m * k_{app} * \Delta t,$$

where  $\Delta x$  = fraction reactor (a segment) ; n, m = reaction order,

$\Delta t$  = residence time per segment = 3600 \* catalyst volume / hourly gas rate.

All reactions are solved in parallel in each reactor segment. Overall conversion is summed across all reactor segments. The user interface is shown in Figure 7.



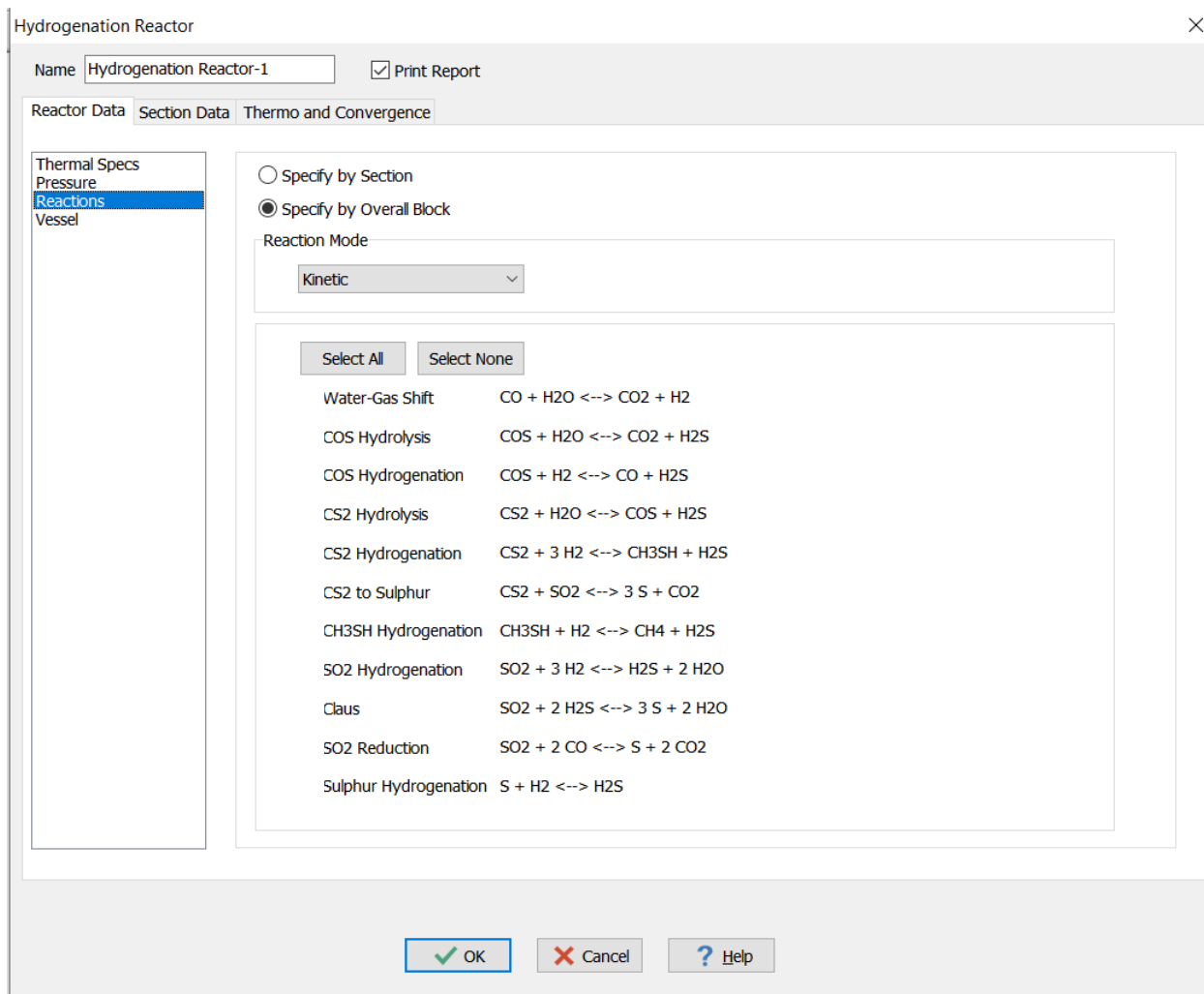


Figure 7 - Hydrogenation Reactor model interface in OGT SulphurPro

## Catalyst Aging and Poisoning Model

Catalyst activity sets the sulfur recovery performance of the TGU. Deactivation of heterogeneous catalysts, such as that used in the TGU hydrogenation reactor, occurs by the processes of aging and poisoning; this is a ubiquitous problem that causes loss of catalytic rate with time. For a comprehensive TGU design, catalyst deactivation over the life of the catalyst charge and its impact on achieving sulfur emission requirements must be addressed.

When fresh catalyst is loaded into the TGU reactor and activated, the catalyst has its maximum surface area and activity. On start-up, the catalyst is immediately exposed to several possible deactivation stresses, causing mostly irreversible damage. Deactivation mechanisms which affect TGU catalyst impact the dispersed active metal sulfide phases of cobalt and molybdenum and the high surface area alumina support. Alumina (and titania) are often used in process industry as support for many heterogeneous catalysts, as well as for the Claus process, so one may draw on that larger body of knowledge as well as being informed by sulfur recovery industry experience.

Activity of these catalysts is strongly related to the  $\gamma$ -alumina (or mixed phase alumina) surface area of the base, alumina crystallites and microporous structure that facilitates accessibility to the reactants. The alumina matrix has hydroxyls on the catalyst surface that serve as weak Brönsted acid sites, promoting hydrolysis and Claus reaction. The extensive surface area supports and interacts with the active cobalt and molybdenum metals.

Activity decline as a function of time and exposure to normal process conditions is treated as aging and is related to loss of surface area and active sites. The remaining fraction active surface area can be represented as an aging factor, AF. Aging tends to occur uniformly throughout the catalyst bed, with catalytic activity or conversion of reactive species declining rapidly at first and then slowly over catalyst life. Spent catalyst activity approaches about 50% of fresh activity and model is fitted to this operating data for aging, as observed in the measurements of Waterton data [4] given in Figure 8:

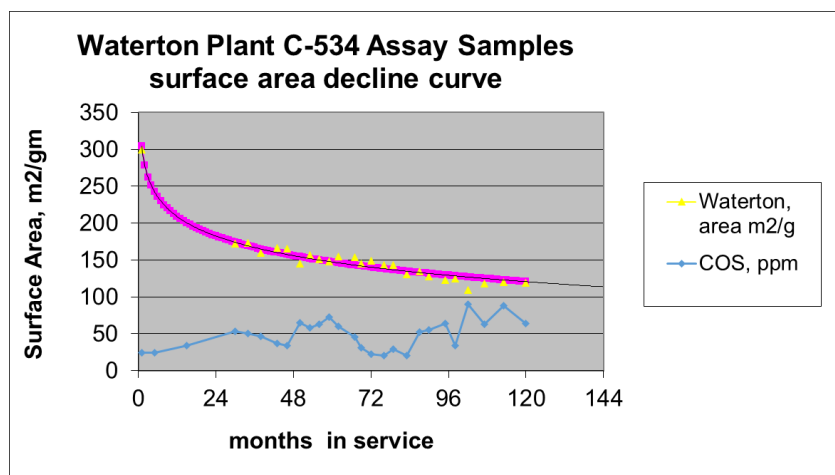


Figure 8 - Waterton (Shell Canada, 1985 – 1995) samples from SCOT reactor, lab data

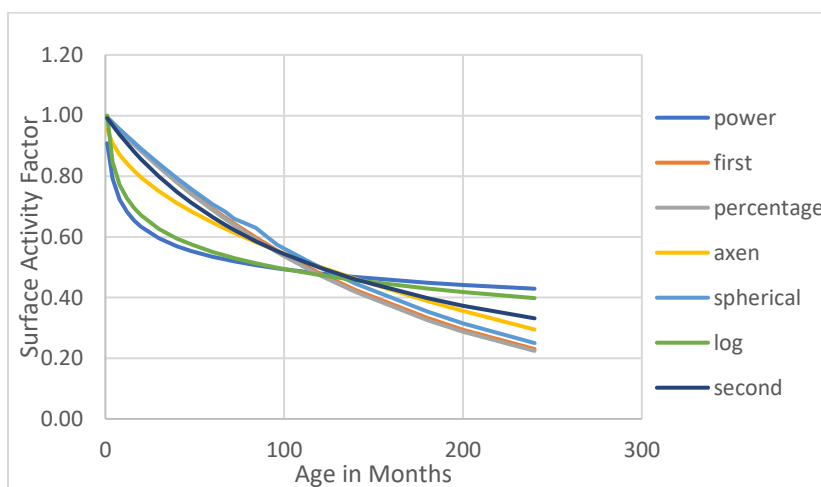


Figure 9 - Various Aging function models

Literature offers several models for aging function. [5] [6] These include classic first order kinetics or second order kinetics, percentage decline, constant rate material transformation with spherical geometry, fractional order (time squared), and various power functions. Figure 9 shows several of these relationships, forces through end point of 50% at 120 months. Early and long term area decline may individually be represented by rational order relationships, however there are only few which fit well the overall activity decline – age function.

Assays of used TGU catalysts report surface area, crush strength, carbon and sulfate [1]. Typically when surface area reaches 120 m<sup>2</sup>/g they are considered spent. Other “spent” criteria are carbon on catalyst is seen at levels approaching one percent; and crush strength decline to half of fresh. Sulfate is not always observed, but on the order of one percent is not unusual, although abused catalyst may have substantial sulfate. Activity testing reported on used catalyst in spent condition expresses about 50% of fresh activity.

Hydrothermal aging is that process which results in transformation, generally the unrecoverable loss of the  $\gamma$ -alumina surface area and activity due to surface smoothing and phase reforming. This process is driven by temperature and water concentration, modifying surface structure through water interaction with hydroxyl groups on alumina. The extent and rate of loss depends on severity of conditions (e.g., exponential with temperature and fractional power of water concentration or humidity.) [6] In the first days or few weeks of operation, significant surface area is lost and activity reduced, after which the surfaces are fairly stable, and area declines slowly over several years. Loss of specific surface area directly impacts catalyst performance as the number of potential Al-OH surface sites drops in proportion to this loss.

Mechanistically, reduced surface area can result from the coalescence of numbers of ultimate particles to form larger spheroidal bodies as well as to the formation of trapped voids rather than catastrophic structural collapse.[6] The process is seen to progress by establishment of filets at contact points and then gradual reformation and merging. For example, coalescence of 8 micro spheres into one result in a single particle with twice the radius and half the surface area.

Generally fresh alumina or TGU catalyst has a specific surface area of 300 – 350 m<sup>2</sup>/g; with initial aging surface area declines to 240 – 260 m<sup>2</sup>/g and then is relatively stable, declining slowly over several years until “spent,” which is at approximately 120 m<sup>2</sup>/g area. Hydrothermal aging tends to occur uniformly throughout the catalyst bed and catalytic activity or conversion of reactive species declines over the useful life, approaching about 50% of fresh activity when spent.

Poisoning is treated as activity loss related to any of several contaminants in the feed. The causes include:

- chemisorption of strongly interactive species,
- reactive contaminants modifying active metal sites, alumina support,
- oxygen slip from burner mal-operation
- fouling, soot, or sulfur
- coking,
- sintering, base structure transformation, or even mechanical damage

Certain streams which wind up at the TGU are known to contribute to this poisoning. Although not ideal for SRU this is sometimes taken as disposal of least consequence. These include:

- reformer hydrogen as supplemental hydrogen, source of BTEX or chlorides
- refinery gas a fuel to RGG, source of BTEX, olefins, heavier hydrocarbon plus variable heating value aggravates RGG sooting or oxygen slip
- acid gas enrichment off-gas (AGE) because it usually contains heavier hydrocarbons and BTEX.

Also, SRUs which process BTEX containing acid gas can pass those species on to the TGU, especially in lean acid gas situations. Impact of BTEX is thought to be reduced at temperatures below 240°C as discussed in several ASRL papers [7].

The poisoning process may proceed through a combination of factors, such as SO<sub>2</sub> chemisorption which then increases acid-site strength, accelerates coking, and blinds active sites. Additionally, oxygen or SO<sub>3</sub> contribute strongly to sulfation. [8] In short, poisoning is degradation that renders the catalyst severely deactivated or inert. Additionally, thermal, or chemical stress from process upsets can cause catastrophic loss of function through destruction of surface area or structure.

It may be useful to consider how deactivation interacts with catalyst pore and active site distribution.[5] Catalytic activity can be defined in terms of the observed external rate constant  $k_{obs}$ , which is equal to the product of the catalyst active site-based intrinsic rate constant  $k_{intr}$ , the effectiveness factor  $\eta$  and the active site density  $\sigma$  (number of sites per area of surface) and aging factor, AF:

$$k_{obs} = k_{intr} * \eta * \sigma * AF$$

Poisoning leads to a loss of active sites, i.e.,  $\sigma = \sigma_0 (1 - \alpha)$ , where  $\alpha$  is the fraction of sites poisoned. The effect on activity is a combination of site density, poison selectivity and mass transfer effects and loss of surface area. Impacts of deactivation are:

- selectivity, how quickly the poison interacts with the catalyst active sites; selective poisoning preferentially affects sites near the pore mouth and slowly progresses along the pore, versus non selective – which progresses more or less uniformly along the entire length of the pore
- $\eta$ , effectiveness factor, reaction rate with mass transfer / intrinsic reaction rates
- $h_T$ , Thiele modulus, ratio kinetic rate to mass transfer rate (diffusion)

The activity response to poisoning depends on the combination selectivity and Thiele modulus. Approximate order is:

- half order for non-selective, large  $h_T$ ;
- first order for ( $h_T$  small, <2),
- reciprocal function ( $1/(1+\sigma \cdot h_T)$ ) (selective,  $h_T$  large)

The catalysts used in TGU service have enhanced pore structures with macro, meso and micro pores. These facilitate good transport of reactants into interior surface and active Co/Mo sites with moderate diffusional resistance. Classic particle geometry estimation of characteristic pore radius and pore length and tortuosity result in rather low value for Thiele modulus and overly conservative estimate of effectiveness factor; experimentally determined comparison of whole and crushed activity coefficients provide the best basis for determination of effectiveness factors.

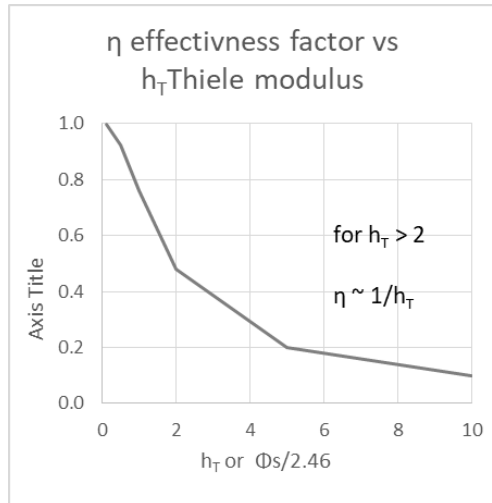


Figure 10 - Effectiveness factor vs Thiele modulus

Impact of poisoning on overall activity is dependent on interaction of effectiveness factor and fraction of sites poisoned. Selective poisoning can have dramatic impact when Thiele modulus is large (strong kinetics and/or diffusional resistance). The linear relationship represents either selective or non-selective poisoning when Thiele modulus is 1 or smaller and was applied selected for the model. Poisoning is seen as occurring at inlet section of reactor bed, due to presence of contaminants and presence of SO<sub>2</sub>, and moving through the bed.

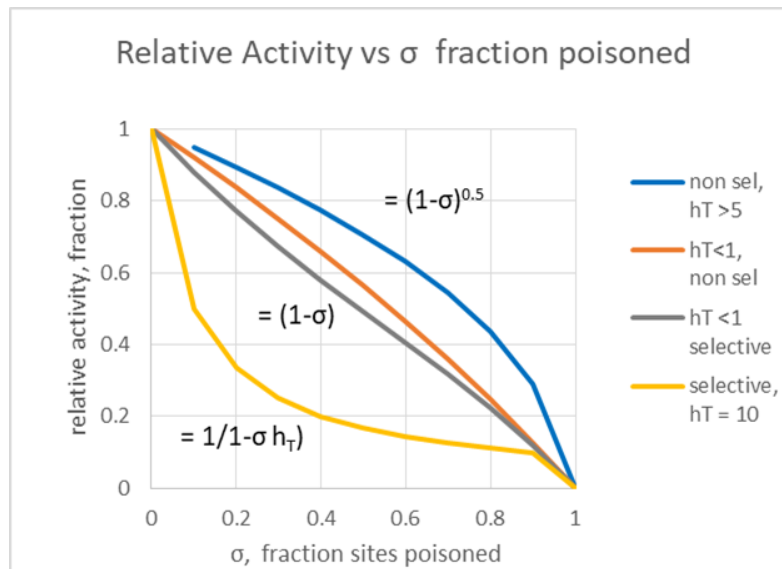


Figure 11 - Relative activity vs Fraction sites poisoned

The effect of poisoning on TGU reactor activity is cumulative, but dependent, on level of poison in feed. Since poisoning mechanisms are driven by concentration, highest at inlet to the reactor or extinguished quickly through reaction, it is therefore taken that poisoning acts at the inlet in a short reaction zone, and progresses through the bed.

A means for forecasting performance across the lifetime of a catalyst charge is provided in the OGT SulphurPro simulation tool. Examples will illustrate application to field observations to interpret operating system temperature profiles. Key causes of deactivation and considerations for mitigation impacts relevant to TGU catalyst are discussed further in the attached reference section.

All these aging and poisoning mechanisms are implemented as decline functions that requires the users to input service run time of the bed along with the exposure to poisoning stresses. The different user configurable poisoning factors include options to specify the use of RGG burner, refinery gas as the fuel source for the burner, reformer hydrogen; an option is provided to specify if the unit processes off-gas from acid gas recovery units. In addition, the interface allows for specifying conditions such as excess air percentage and the quantity of BTEX in the feed gas. All these options together construct a poisoning factor that is built into the mathematical framework of the catalyst bed. The SulphurPro user interface for specifying the aging and poisoning level are shown in Figure 12.

The image displays two side-by-side dialog boxes from the OGT SulphurPro software interface.

The left dialog box, titled "Catalyst Aging", contains a "Months" input field with the value "20" and a "Catalyst Age Parameter" input field with the value "0.917". Below these fields is a vertical slider bar with a blue handle. The top of the slider is labeled "0.0" on the left and "1.0" on the right. The bottom of the slider is labeled "240.0" on the left and "0.0" on the right. At the bottom of the dialog are "OK", "Cancel", and "Help" buttons.

The right dialog box, titled "Catalyst Poisoning", contains several checkboxes: "Burner" (checked), "Refinery Gas" (unchecked), "Air Slip / Excess Air" (unchecked) with a percentage input field, "Reformer Hydrogen" (unchecked), "BTEX" (unchecked) with a "ppm" input field, and "Acid Gas Enrichment Off-Gas" (unchecked). Below these options is a box displaying "Poisoning Parameter: 2". At the bottom of the dialog are "OK", "Cancel", and "Help" buttons.

Figure 12 - OGT SulphurPro interface for specifying catalyst age and poisoning level

## Model Case Study

To study the usability of the model, a case study was performed by running the hydrogenation reactor model on a typical tail gas reactor feed at various levels of catalyst aging and poisoning.

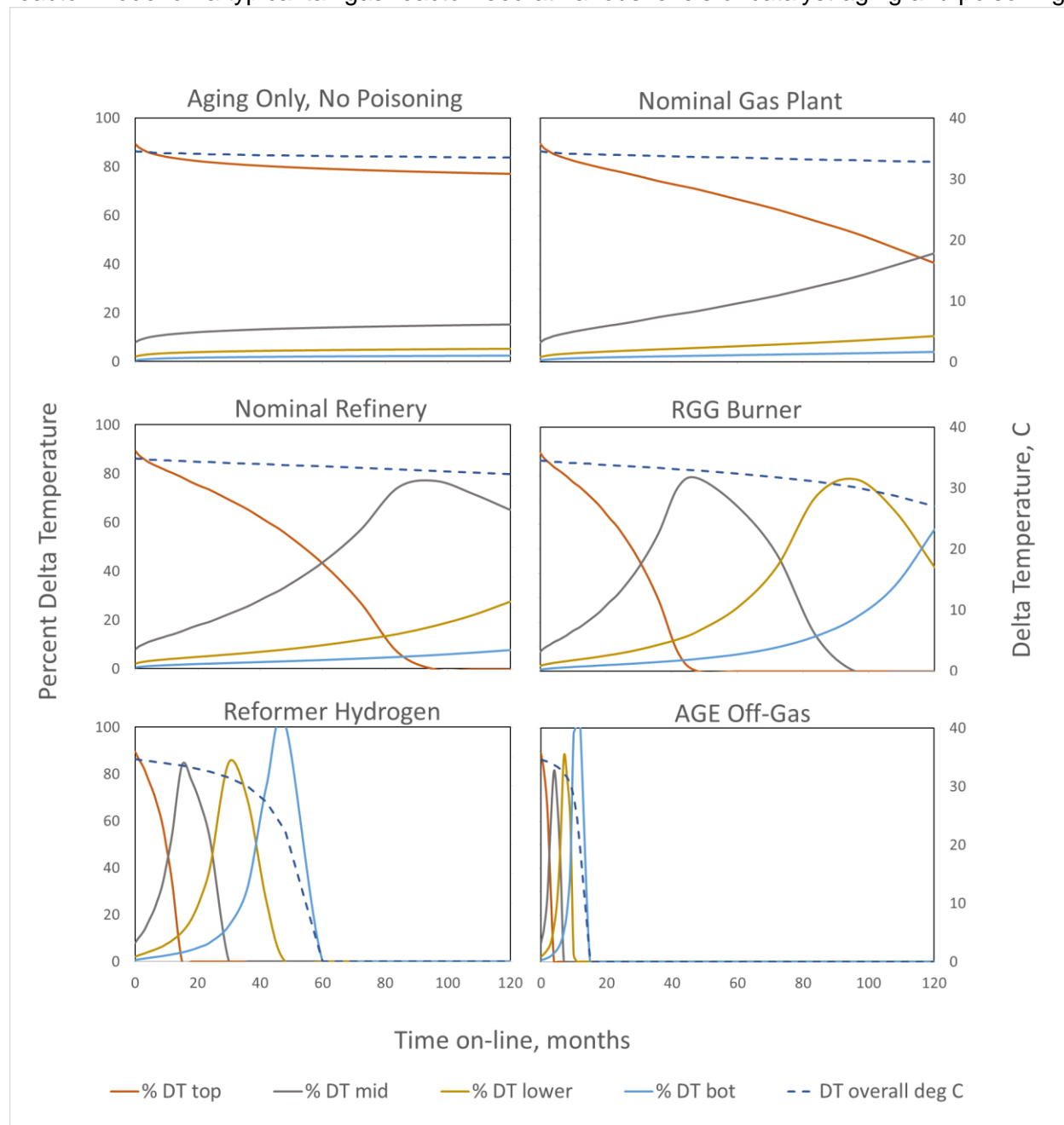


Figure 13 shows the temperature profile of the bed as a function of catalyst age at different poisoning conditions. The x-axis denotes the time online in months, the major y-axis denotes the percentage temperature rise that occurs in each quarter of the bed and the secondary y-axis gives the total temperature rise across the catalyst bed. Each plot refers to the different poisoning mechanisms. Note these profiles show four zones, but the bottom zone (lower bed to outlet) in most operating units is disregarded because heat losses accrue here and DT is often negative.



The poisoning situations that were studied include an idealized operating scenario which has no poisoning sources, the expected poisoning of a gas plant and a refinery operating with a clean source of hydrogen, units with an inline RGG burner, reformer hydrogen and a TGU processing the off-gas from an Acid Gas Enrichment (AGE) unit. For the same runs, Figure 14 shows the outlet concentration of various sulfur species. Here the curves represent the different poisoning cases and each sulfur bearing species are shown in individual plots.

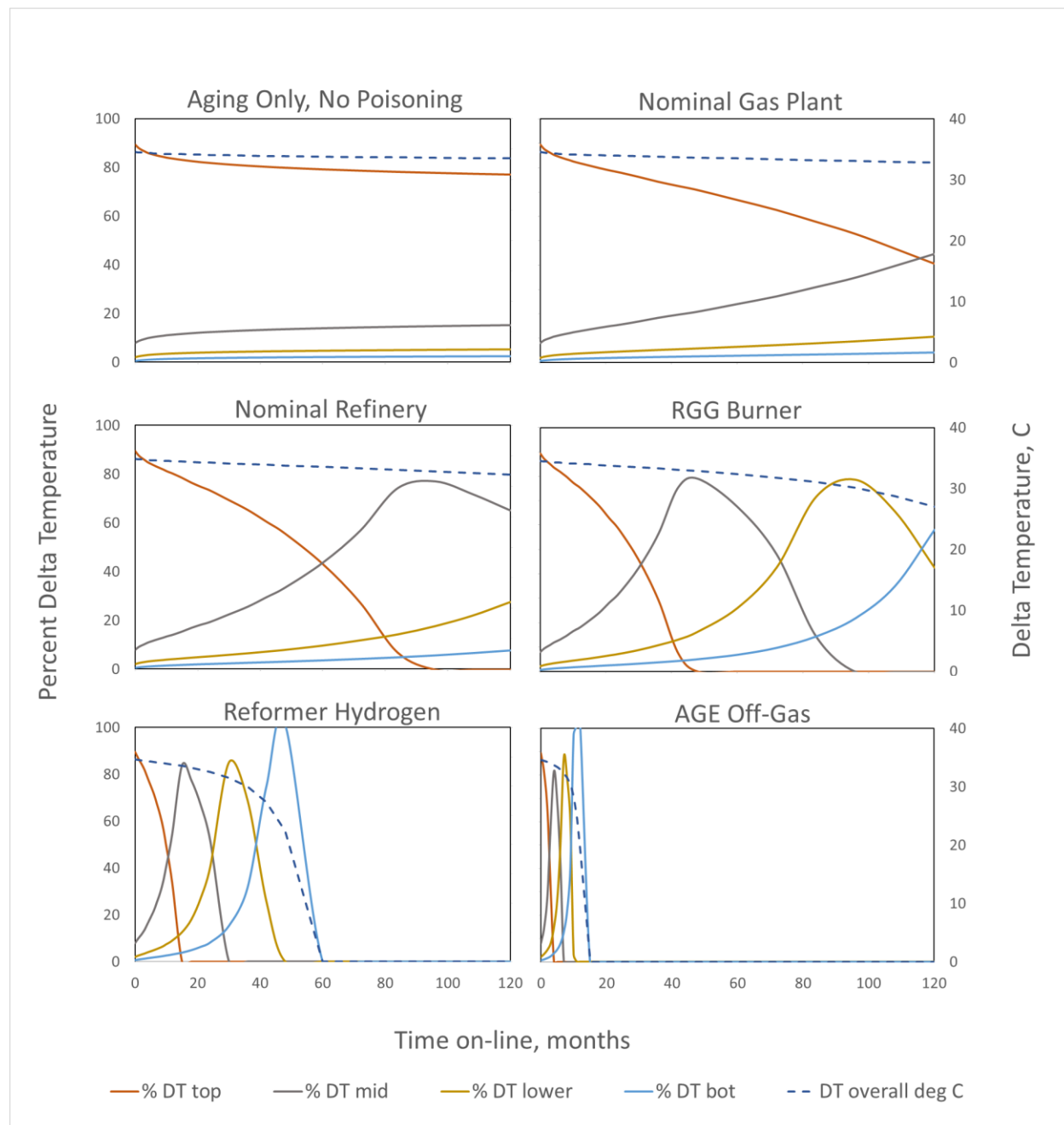


Figure 13 - Reactor temperature profile as a function of catalyst age at various poisoning levels

It is important to note, as the temperature profiles indicate, for the idealized case with no poisoning, almost all the exotherm still occurs in the top quarter of the bed even for fully aged catalyst. Slip of non-H<sub>2</sub>S sulfur compound increases from 25 ppm for fresh to 100 ppm for fully aged catalyst because catalyst activity is reduced to expected spent level of half fresh, with conversion decreasing for all reactions. The exotherm shift typically observed in operations reflects poisoning the top of bed, effectively reducing the amount of catalyst and conversion, further increasing sulfur slip.

Exposure to mild levels of contaminants that would be encountered in a gas plant or a refinery and moderate levels that would be expected with a unit that is operating on a RGG burner, shifts the exotherm away from the top of the bed as the catalyst at the inlet is deactivated by poisons. At shorter operating periods a less deactivated catalyst offsets the impact of poisoning and moderates sulfur slip. In the latter two cases, the model predicts the first quarter of the bed gets deactivated completely after around 100 months and 40 months, respectively. These poisoning contributions leave very little room for other plant upsets and shorten the operating lifetime. In the most severe cases, Reformer Hydrogen or AGE Off-Gas, it precludes even meeting typical turnaround objectives of 3-5 years (36-60 months).

As shown in Figure 14, in the case of Reformer Hydrogen and AGE Off-Gas, the bed activity declines rapidly compared to the other cases owing to the significant levels of contaminants in the feed, being exhausted at around 60 months and 20 months, respectively. with even shorter useful operating life.

Corresponding outlet concentration plots indicate the onset of trace sulfur slippage from COS and mercaptans in addition to carbon monoxide. All these compounds typically escape the TGU amine loop and reach the Thermal Oxidizer, thus increasing emissions.

In the severely poisoned cases, SO<sub>2</sub> slip is also occurring early in the life cycle. As discussed previously, even trace amounts of SO<sub>2</sub> slip can lead to its gradual accumulation in the quench system and TGU amine loops downstream. SO<sub>2</sub> being a relatively strong acid (compared to the reduced sulfur compounds) can severely reduce the amine solvent's capacity in removing other acid gases which in turn increases the overall emissions. Furthermore, the buildup of SO<sub>2</sub> can lead to severe fouling and corrosion issues in the quench system. The rigorous high-fidelity kinetic model can help designers and operators forecast the life expectancy of the catalyst bed.

The internal composition profiles of the reactor bed for various species of interest are shown in Figure 15, which otherwise would not be available from normal operating data. For fresh catalyst, all the SO<sub>2</sub> is converted in just the first 20% of the bed. This increases to 40% at 48 months with no poisoning and to 60% with an RGG burner for a 48-month aged catalyst. The significance of water gas shift reaction as a source of hydrogen can be inferred from the minima in the H<sub>2</sub> concentration profile. The initial sudden drop can be attributed to the fast reduction of SO<sub>2</sub> to H<sub>2</sub>S, which stoichiometrically consumes 3 moles of hydrogen per mole of SO<sub>2</sub> converted. The hydrogen concentration then gradually starts increasing from the conversion of carbon monoxide by the water gas shift reaction. This, in addition to providing a hydrogen source for the reduction of trace sulfur species ensures that the carbon monoxide emissions are reduced.

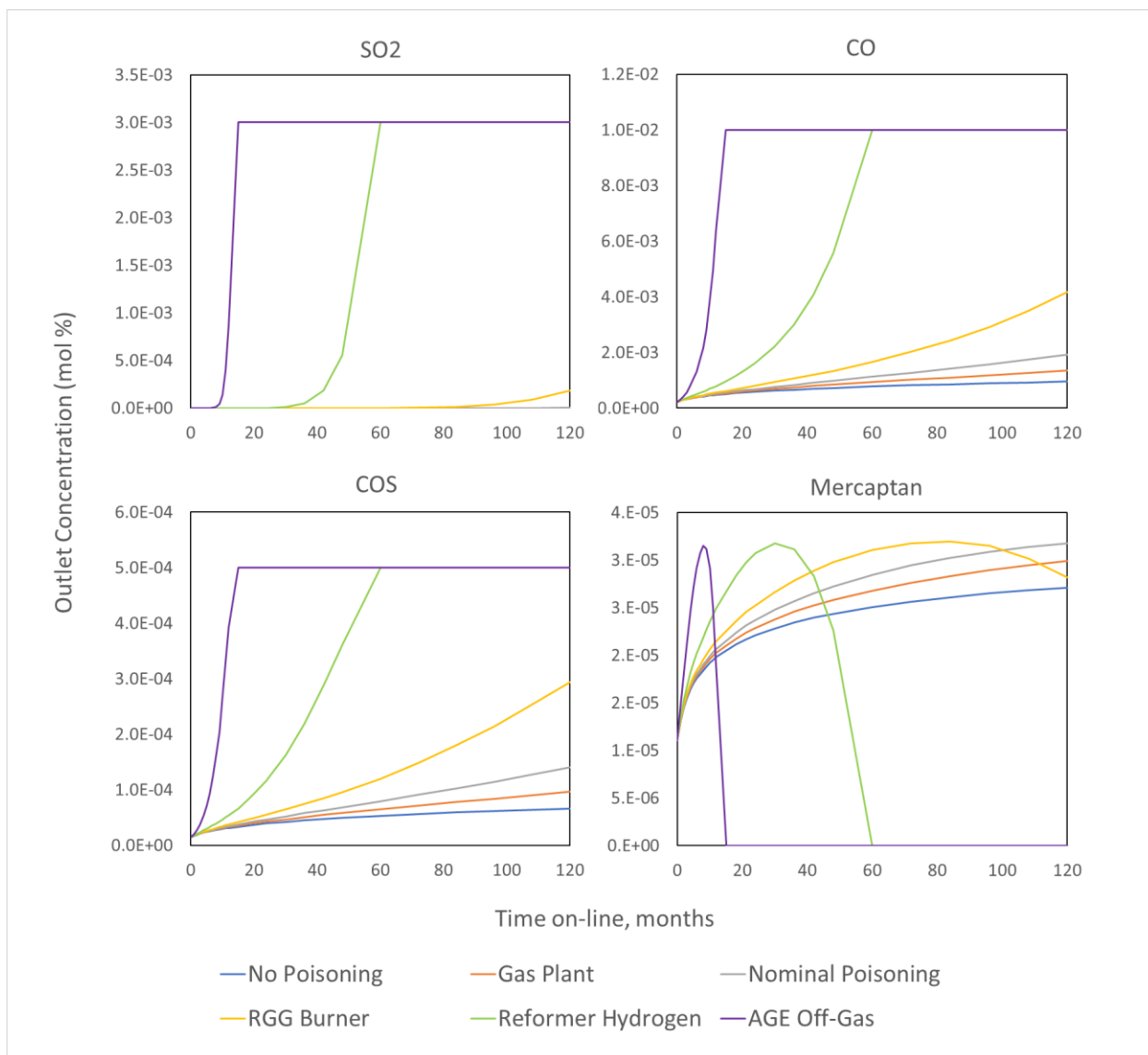
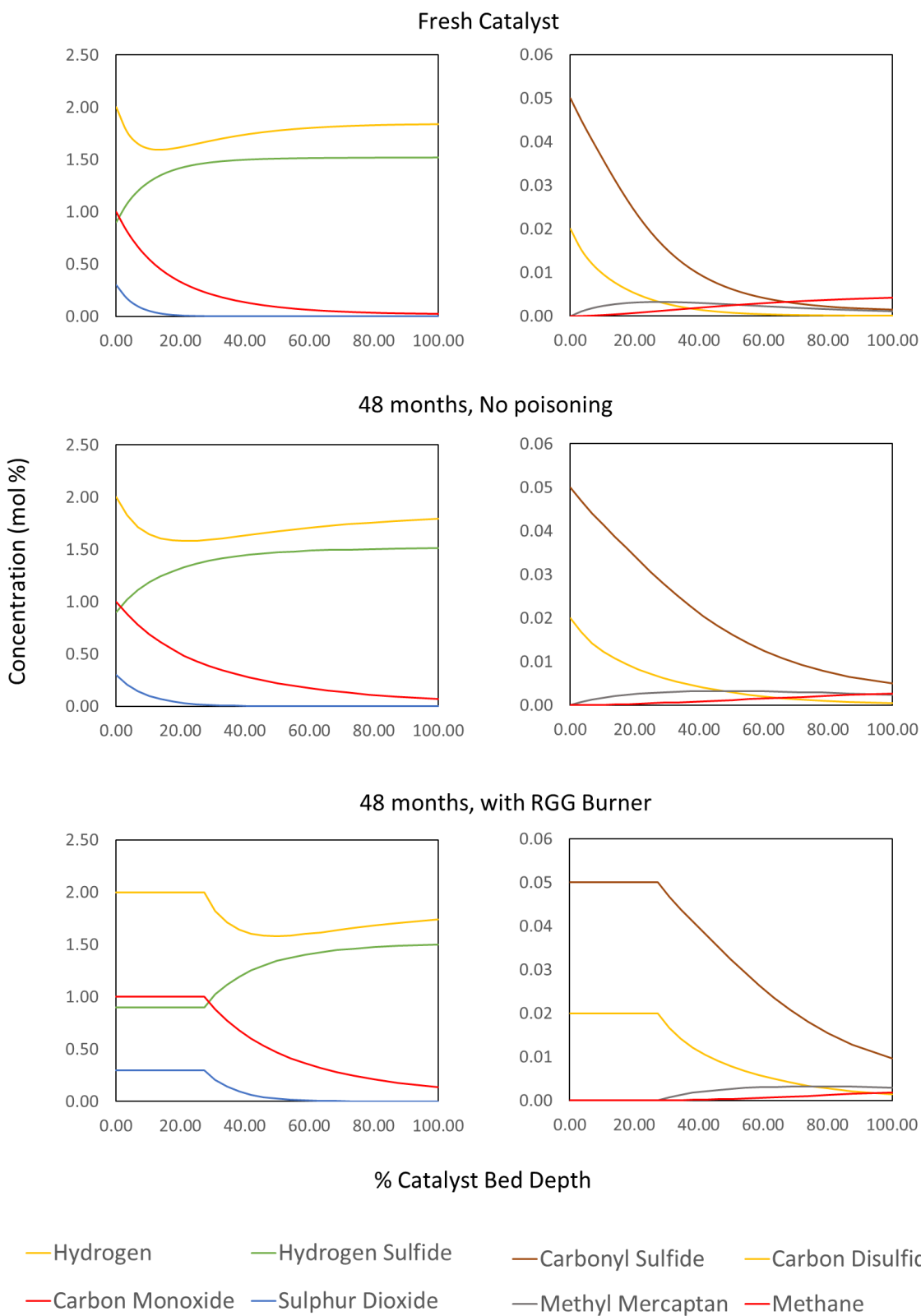


Figure 14 - Reactor Outlet Gas Concentrations as a function of catalyst age at various poisoning levels

The concentration of mercaptan increases along with the bed depth initially as it is an intermediate of CS<sub>2</sub> reaction, but it is later hydrogenated thus keeping the outlet concentration low. However, as activity decreases from aging and poisoning, mercaptan concentration increases as it is still formed from CS<sub>2</sub> (which is still almost completely converted), but the degree of intermediate RSH destruction declines as the active portion of bed shrinks. Total sulfur slippage (represented as total of all sulfur atoms in COS, CS<sub>2</sub>x2 and RSH) typically slip past amine system to Thermal Oxidizer. Both aging and poisoning have impact on sulfur slip as seen for fresh and 48-month conditions:

- Fresh ~26 ppmv
- Aging only at 48 months ~83 ppmv
- Refinery + RGG at 48 months ~153 ppmv



*Figure 15 - Reactor composition profiles*

Note that this analysis does not consider that there may be additional plant-specific factors. First, the analysis is limited to a typical TGU feed with 1<sup>st</sup> Generation Co/Mo hydrogenation catalyst. Improved catalysts may be available at some sites. Secondly, a robust TGU design will provide the operators some flexibility for increasing the reactor inlet temperature to compensate for some of the slower reactions. The penalties for this flexibility are incremental fuel or energy usage (cost) and increased baseline hydrothermal aging of the catalyst. Both of these factors can be studied with the use of the OGT SulphurPro model.

## Conclusions

Sound technical tools, which represent kinetics of the TGU system and enable meaningful simulation, aids one to see substantial impact on performance and can identify and mitigate a serious event before it happens.

A hydrogenation reactor which has aging only would have most of the temperature rise in top zone even at end of catalyst life. Some degree of poisoning is indicated for most units as they witness operating temperature profiles shifting into middle and bottom zones across life cycle.

The temperature profile of a TGU hydrogenation reactor provides useful insight to performance and catalyst health. TGU hydrogenation reactor catalyst deactivation is caused by aging and poisoning. Deactivation is inevitable, and generally irreversible. Catalyst deactivation reduces conversion and increases slip of non H<sub>2</sub>S compounds; in severe cases SO<sub>2</sub> may slip causing corrosion, fouling and equipment damage. Poisoning reduces conversion, increases sulfur slip and may shorten catalyst life cycle.

The model presented not only captures the detailed reaction kinetics, but also accounts for deactivation from aging (depending on temperature, humidity, and time) and poisoning (related to operational stresses, e.g., BTEX or O<sub>2</sub> in feed). Hydrothermal aging affects the relative activity of an entire bed, whereas poisoning impacts the bed along the flow path, starting at the inlet and moving toward the outlet. Poisoning accelerates performance decline, related to loss of conversion of sulfur species that slip through TGU to the Thermal Oxidizer.

All operators aspire to achieve longevity in catalyst service. With this information it is possible to recognize what is an achievable decline in catalyst activity and what is more severe decline through analysis of operation. When modeling with appropriate aging and poisoning factors there is the opportunity to use the knowledge provided by the model to decide whether to intervene to remove poison or plan appropriately to make timely replacement of catalyst.

With all those elements considered, one can use the model to analyze and predict the performance and useful life of a real reactor based on comparison of simulated vs. actual temperature profiles, especially over time. So, designers will have a tool to better specify reactors and operators will be better able to quantify what is actually occurring instead of only simulating ideal operation.

Improved operation and better designs can reduce sulfur emissions, improving quality of life.

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## Appendix - Catalyst Deactivation

Catalyst deactivation, the loss over time of catalytic activity and/or selectivity, is a problem of great and continuing concern in the practice of industrial catalytic processes. Costs to industry for catalyst replacement and process shutdown total billions of dollars per year, and in the sulfur recovery field TGU catalyst expenses are on the order of \$50 million per year plus associated cost of unloading and loading. This does not consider the lost profit from downtime for unplanned outages, which can exceed \$1 million per day at a sulfur constrained facility. Ensuring that the catalyst operates well and for its full potential is of value to the industry as well as avoiding unnecessary or early change out.

Time scales for catalyst deactivation vary considerably; for example, in the case of cracking catalysts, catalyst mortality may be on the order of seconds, while in ammonia synthesis the iron catalyst may last for 5 – 10 years. However, it is inevitable that all catalysts will decay. In the TGU field typical life is 5 – 6 years, although many operators can operate a charge through two turnaround cycles and have successfully operated for 10 – 12 years. Severe cases of deactivation have shortened life to a few months, though most make a normal operational cycle of 3 – 4 years. There are two long-term records, 18 years and 20 years, which are exceptional results.

Deactivation and degradation can be classified by stress type: chemical, thermal, and mechanical. Mechanisms are multiple: poisoning, coking, fouling, thermal degradation/sintering, vaporization or sublimation, metal/support interactions, and attrition/crushing. Typically, the loss of activity in a well-controlled process occurs slowly. However, process upsets or poorly designed hardware can bring about rapid, catastrophic failure.

Many are the paths for heterogeneous catalyst decay. For example, a catalyst solid may be poisoned by any one of several contaminants present in the feed. Its surface, pores, and voids may be fouled by carbon or coke produced by cracking/condensation reactions of hydrocarbon reactants, intermediates, and/or products. The presence of oxygen or chlorine in the feed gas can lead to formation of volatile oxides or chlorides of the active phase, followed even by gas-phase transport from the reactor. Similarly, changes in the oxidation state of the active catalytic phase can be induced by the presence of reactive gases in the feed, for example  $O_2$  or  $SO_3$ . In the following sections the mechanisms pertinent to TGU catalysts are discussed.

The sections which follow are drawn from several references, available for more detailed examination of deactivation mechanisms, as well as experience in the sulfur recovery industry:

Hydrothermal Aging of Silica-Alumina Cracking Catalysts by Arpad Elo, Jr., and Porter Clements Catalyst Division, Nalco Chemical Company, Chicago, Illinois 60629, Journal Physical Chemistry 1967

*Heterogeneous Catalyst Deactivation and Regeneration: A Review* Catalyst 2015; Morris D. Argyle and Calvin H. Bartholomew



## Hydrothermal Aging

Hydrothermal aging is an unavoidable deactivation mechanism that causes an unrecoverable loss in surface area of alumina or titania. The overall mechanism is one of surface transformation, modifying surface structure through water interaction with hydroxyl groups on alumina. Significant surface area is lost and activity reduced in the first days to few weeks of operation, depending on severity of conditions, e.g. temperature and water concentration.

The surface of fresh catalyst has many imperfections, creating large area and active sites. Reformation occurs early in operation, reducing surface energy and stabilizes at about a 30% reduction in area, after which the surface is stable, declining slowly over years. Through this mechanism  $\gamma$ -alumina, a crystalline form with high specific surface area with aluminol groups (acidic sites: hydroxyl/quatra-valent aluminum atoms) is converted to ( $\beta$ -Al(OH)<sub>3</sub>) boehmite, bayerite or gibbsite. (J Physical Chemistry, 1957) Surface hydroxyls can also condense to dehydroxylate the surface. Also, diffusion of surface Al atoms results from the breakage and reestablishment of surface Al-O-Al bonds. Loss of specific surface area directly impacts catalyst performance as the number of potential Al-OH surface sites drops in proportion to this loss.

Mechanistically reduced surface area results from the coalescence of numbers of smaller particles to form larger spheroidal bodies as well as to the formation of trapped voids rather than catastrophic structural collapse. The process is seen to progress by establishment of filets at contact points and then gradual reformation and merging. For example, coalescence of 8 micro spheres into one result in a single particle with twice the radius and half the surface area.

Active metals can also migrate or undergo crystallite growth under hydrothermal conditions, reducing active site density. Water vapor promotes sublimation or migration, which acts to grow larger crystallites or slabs, reducing dispersion and with fewer sites, lower activity results. The sulfide form is less volatile and more resistant to migration than the oxide form.

Generally fresh alumina or TGU catalyst has a specific surface area of 300 – 350 m<sup>2</sup>/g, which rapidly declines to 240 – 260 m<sup>2</sup>/g and then is relatively stable, declining slowly over several years until “spent,” which is at approximately 120 m<sup>2</sup>/g area. Hydrothermal aging tends to occur uniformly throughout the catalyst bed and catalytic activity or conversion of reactive species declines over the useful life, approaching about 50% of fresh activity when spent.

## Thermal Degradation and Sintering

Sintering is the name generally applied to a thermal process which causes (fairly rapid) agglomeration of base (micro) particles in substrate or agglomeration of active metals. Hydrothermal aging is subset of chemically assisted sintering, a specialized form of sintering at lower temperatures driven by water vapor as well as temperature. The sulfide form of the active metals is fairly stable and provides some resistance to sintering as sublimation temperatures are higher than for the oxides. Temperature exposure that causes sintering (500 – 1000 C) is usually well above normal operating range for a TGU, but is experienced in some units with upset conditions, especially introduction of oxygen.

Thermally induced deactivation of catalysts results from (1) loss of catalytic surface area due to crystallite growth of the catalytic phase, (2) loss of support area due to support collapse and of catalytic surface area due to pore collapse on crystallites of the active phase, and/or (3) chemical transformations of catalytic phases to non-catalytic phases.

Steam and thermal deactivation are believed to occur by means of separate mechanisms, differing primarily in the mode of mass transport. In the presence of steam, a surface diffusion or vapor phase transport process predominates, whereas in the absence of steam a bulk diffusion process predominates as well as grain boundary diffusion. It is suggested that the trapping of voids within catalysts steamed to low surface areas may be considerable (Journal of Physical Chemistry, *Hydrothermal Aging of Silica-Alumina Cracking Catalysts* by Arpad Elo, Jr., and Porter Clements, Nalco Chemical Company, 1967)

There is a pseudo-mechanical aspect to aging from thermal cycling. Temperature changes in the presence of water vapor cause constant expansion and contraction of the catalyst, warping and misshaping its surface, and causing a permanent destruction of micropore structure. This is a normal aging process for the catalyst and occurs over an extended period. The crush strength is reduced and some attrition occurs, producing fines.

Sintering processes generally take place at high reaction temperatures (e.g., > 500 °C) and are generally accelerated by the presence of water vapor. Sintering and redispersion has focused on supported metals. Three principal mechanisms of metal crystallite growth have been advanced: (1) crystallite migration, (2) atomic migration, and (3) (at very high temperatures) vapor transport.

Sintering rates increase exponentially with temperature. Metals sinter relatively rapidly in oxygen and relatively slowly in hydrogen. Sintering rates are exponentially dependent on T;  $E_{act}$  varies from 30 to 150 kJ/mol. Each decreases with increasing metal loading and increases in the following order with atmosphere:  $NO < O_2 < H_2 < N_2$ . Metal-support interactions are weak (bond strengths of 5–15 kJ/mol); with a few exceptions, thermal stability for a given metal decreases with support in the following order:  $Al_2O_3 > SiO_2 > carbon$ .

The effect of temperature on sintering of metals and oxides can be understood physically in terms of the driving forces for dissociation and diffusion of surface atoms, which are both proportional to the fractional approach to the absolute melting point temperature ( $T_{mp}$ ). Thus, as temperature increases, the mean lattice vibration of surface atoms increases; when the Hüttig temperature ( $0.3T_{mp}$ ) is reached, less strongly bound surface atoms at defect sites (e.g., edges and corner sites) dissociate and diffuse readily over the surface, while at the Tamman temperature ( $0.5T_{mp}$ ), atoms in the bulk become mobile. Accordingly, sintering rates of a metal or metal oxide are significant above the Hüttig temperature and very high near the Tamman temperature. Data set presented below is for compounds of cobalt and molybdenum, active metals in TGU catalysts.

Compound	T <sub>mp</sub> , K	T Tamman, K	T Hüttig, K
Co	1753	877	526
CoO*	2206	1103	662
CoS	1468	734	440
CoCl <sub>2</sub>	1008	504	302
Mo	2883	1442	865
MoO <sub>3</sub>	1068	534	320
MoS <sub>2</sub>	1458	729	437
Mo <sub>2</sub> Cl <sub>10</sub>	467	233	140

\*Cobalt also forms a mixed oxide, Co<sub>3</sub>O<sub>4</sub> with mp = 1250K

For reference, operating temperature of TGU reactor is 200 – 300 C, or 473 – 573K.

Promoters or impurities affect sintering and redispersion by either increasing (e.g., chlorine and sulfur) or decreasing (e.g., oxygen, calcium, cesium) metal atom mobility on the support; in the latter case, this is due to their high resistance to dissociation and migration due to high melting points, as well as their hindering dissociation and surface diffusion of other atoms. Similarly, support surface defects or pores impede surface migration of metal particles—especially micropores and mesopores with pore diameters about the same size as the metal crystallites.

Sintering rate data were historically fitted to a simple power-law expression (SPLE) of the form:

$$\frac{d\left(\frac{D}{D_0}\right)}{dt} = k_s \left(\frac{D}{D_0}\right)^n$$

where  $k_s$  is the sintering rate constant,  $D_0$  the initial dispersion, and  $n$  is the sintering order, which for typical catalyst systems may vary from 3 to 15. Unfortunately, the SPLE assumes that surface area or dispersion ultimately reaches zero, given sufficient time, when in fact, for a given temperature and atmosphere, a non-zero or limiting dispersion is observed.

The general power-law expression (GPLE) adds a term account for the observed asymptotic approach of the typical dispersion versus time curve:

$$\frac{d\left(\frac{D}{D_0}\right)}{dt} = k_s \left(\frac{D}{D_0} - \frac{D_{eq}}{D_0}\right)^m$$

This results in a limiting dispersion  $D_{eq}$  at infinite time. The order of sintering,  $m$ , is found to be either 1 or 2. Fuentes and Bartholomew.

References give example rates and activation energies (temperature dependence) although TGU catalysts are not explicitly included.

There is direct evidence from the previous studies of model-supported catalysts [104,107] for the occurrence of crystallite migration (mainly in well-dispersed systems early in the sintering process), atomic migration (mainly at longer sintering times), and spreading of metal crystallites (mainly in oxygen atmosphere). There is also evidence that under reaction conditions, the surface is dynamic, i.e., adsorbates and other adatoms rapidly restructure the surface and slowly bring about faceting; moreover, thermal treatments cause gradual changes in the distribution of coordination sites to minimize surface energy. There is a trend in increasing sophistication of spectroscopic tools used to study sintering and redispersion. In the next decade, we might expect additional insights into atomic and molecular processes during reaction at the atomic scale using STM, analytical high resolution transmission electron microscopy (HRTEM), and other such powerful surface science tools.

Single-phase oxide carriers sinter by one or more of the following processes: (1) surface diffusion, (2) solid-state diffusion, (3) evaporation/condensation of volatile atoms or molecules, (4) grain boundary diffusion, and (5) phase transformations. In oxidizing atmospheres,  $\gamma$ -alumina and silica are the most thermally stable carriers; in reducing atmospheres, carbons are the most thermally stable carriers. Steam accelerates support sintering by forming mobile surface hydroxyl groups that are subsequently volatilized at elevated temperatures. Chlorine also promotes sintering.

## Sulphur Condensation / Sulfur Fouling

If the reactor is operated at or below the sulfur dewpoint, liquid sulfur can accumulate within the catalyst's pores, blocking access. This is typically associated with a problem in the upstream SRU coalescer operation or a blocked rundown line. It is also notable that sulfur condensation within the micropore structure is possible because the bulky  $S_8$  molecule formed is larger than some of the micropores.

Whereas  $SO_2$  is converted to sulfur and water on Co/Mo active sites, the resulting sulfur atom is still adsorbed on the Co/Mo sites and is hydrogenated on to  $H_2S$ . However, if  $SO_2$  conversion is achieved via the Claus reaction on alumina, this results in a  $S_6$  or  $S_8$  molecule which must desorb, diffuse and re-adsorb on Co/Mo to be converted to  $H_2S$ . The  $S_8$  molecule can effectively become irreversibly stuck, and being unable to vacate the catalyst pore, condenses and blocks the pore. This can be reversed simply by increasing the temperature within the bed, to re-vaporize the condensed sulfur. Sometimes, this is easier said than done. For example, the designer may have failed to provide enough margin to the preheater to cover this operating scenario or is restricted to using condensing steam which limits the temperature.

Excessive sulfur entrainment from upstream SRU condensers/coalescers or blocked sulfur rundown lines can also increase the likelihood of reaching the sulfur dewpoint within the catalyst bed (not just in the catalyst pore). SulphurPro® evaluates the dewpoint temperature margin within the catalyst bed, which is crucial to predicting deactivation by this mechanism.

## Carsul

Carsul is akin to coking coincident with polymerization, adding a yet another dimension to hydrocarbon contamination in the TGU. When  $C_3+$  hydrocarbons enter the TGU reactor they can crack on the catalyst's acid sites and combine with sulfur across the catalyst surface, forming a tenacious carbon-sulfur polymer (hence the term Carsul). Like sooting, this coats the catalyst, blocks the macropores and prevents access to the mesopores and micropores. Cracking tendency is worst at high operating temperatures, especially above 450°F (232°C). BTEX is particularly nasty in this regard as the cracking occurs deeper in the catalyst pore structure. Carsul formation can occur with any  $C_3+$  hydrocarbon. Again, high acidity and the presence of  $SO_2$  drives this reaction, and presence of sulfur is required, so it tends to form from the reactor inlet progressively down through the bed.

Deactivation by Carsul is permanent, but it is completely preventable by keeping precursor hydrocarbons out of the feed. Certain streams are known to contribute to this headache, including utilizing reformer hydrogen as supplemental hydrogen, refinery gas a fuel to RGG, and processing acid gas enrichment off-gas (AGE) because it usually contains heavier hydrocarbons and BTEX. Also, sulfur plants which process BTEX can pass those species on to the TGU, especially in lean acid gas situations because of the challenge to produce Reaction Furnace temperatures which are high enough to destroy BTEX. Activated carbon and silica gel beds have historically been used to scavenge BTEX out of lean acid gas feeds to the SRU.

## Sulfation

Sulfation results from the interaction of  $SO_2$  and  $H_2O$  on the catalyst surface, causing gradual buildup of sulfate. It reduces the effective surface area of the catalyst. In the TGU,  $SO_2$  concentrations are low and  $SO_2$  is fully converted across the reactor bed. The strong chemisorption of  $SO_2$  is generally reversible, but inhibits hydrolysis of COS and  $CS_2$ .  $SO_2$  raises

acidity which promotes coking, and with oxygen slip forms sulfate which is permanent. If  $\text{SO}_3$  is present it will sulfate the alumina.

Poisoning is the strong chemisorption of reactants, products, or impurities on sites otherwise available for catalysis. Thus, poisoning has operational meaning; that is, whether a species acts as a poison depends upon its adsorption strength relative to the other species competing for catalytic sites. For example, oxygen can be a reactant in partial oxidation of ethylene to ethylene oxide on a silver catalyst and a poison in hydrogenation of ethylene on nickel. In addition to physically blocking of adsorption sites, adsorbed poisons may induce changes in the electronic or geometric structure of the surface. Finally, poisoning may be reversible or irreversible. An example of reversible poisoning is the deactivation of acid sites (in fluid catalytic cracking catalysts) by nitrogen compounds (ammonia, cyanide) in the feed. Regardless of whether the poisoning is reversible or irreversible, the deactivation effects while the poison is adsorbed on the surface are the same. Many poisons occur naturally in feed streams that are treated in catalytic processes.

Refinery units process crude oil which contains sulfur and metals, such as vanadium and nickel, arsenic phosphorous, and selenium, zinc that act as catalyst poisons for many petroleum refinery processes; these can enter off gas streams from those units and make their way into refinery gas or the acid gas removal units. Although most of these metal poisons wind up on the catalysts in the units where they are processed, some migrate or are entrained into the vapor phase and make their way into the acid gas and the SRU.

Fouling is the physical (mechanical) deposition of species from the fluid phase onto the catalyst surface, which results in activity loss due to blockage of sites and/or pores. Important examples include mechanical deposits of carbon and coke in porous catalysts as well as condensation of sulfur. Carbon and coke forming processes also involve chemisorption of different kinds of carbons or condensed hydrocarbons that may act as catalyst poisons. Carbon can be a product of CO disproportionation while coke is produced by decomposition or condensation of hydrocarbons (aromatic / BTEX, olefins, and heavier hydrocarbons) on catalyst surfaces and typically consists of polymerized heavy hydrocarbons. Nevertheless, coke forms may vary from high molecular weight hydrocarbons to primarily carbons such as graphite, depending upon the conditions under which the coke was formed and aged.

## Coking

Carbon and coke formation on supported metal catalysts can restrict access via build-up on active metal sites or support, or blind active metal sites. Carbon may (1) chemisorb strongly as a monolayer or physically adsorb in multilayers and in either case block access of reactants to metal surface sites, (2) totally encapsulate a metal particle and thereby completely deactivate that particle, and (3) plug micro- and mesopores such that access of reactants is denied to many crystallites inside these pores.

Coking is accelerated on super acid sites, which sites are a result of  $\text{SO}_2$  adsorption or sulfate formation, in the upper portion of bed before,  $\text{SO}_2$  is extinguished. This is especially impactful where aromatics, heavy hydrocarbons or olefins are present. Hydroxyls on the catalyst surface serve as weak Brönsted acid sites with acid strength inversely proportional to the O-H bond

strength. Sulfur dioxide additionally pulls electron density away from the O-H bond, making the H sufficiently acidic to catalyze the coking.

Deactivation of supported metals by carbon or coke may occur chemically, owing to chemisorption or carbide formation, or physically and mechanically, owing to blocking of surface sites, metal crystallite encapsulation, plugging of pores. Destruction of catalyst pellets by carbon filaments occurs in other applications but has not been observed in TGU applications. Blocking of catalytic sites by chemisorbed hydrocarbons, surface carbides, or relatively reactive films is reversible in regeneration with controlled oxidation, although seldom practiced.

In addition to hydrocarbon structure and reaction conditions, both the extent and rate of coke formation are also a function of the acidity and pore structure of the catalyst. Generally, the rate and extent of coke formation increases with increasing acid strength and concentration. For this reason, coking is driven in part by SO<sub>2</sub> presence, which increases acidity of alumina, and therefore coking will be more severe in the top of the bed and/or at the first active reaction front. Coking in TGU catalyst will proceed from top to bottom of the bed, but can also occur thorough out the bed to some degree.

The principal chemical loss of activity in oxides and sulfides is due to the strong adsorption of coke molecules on acidic sites. Strong acid sites also play an important role in the formation of coke precursors, which subsequently undergo condensation reactions to produce large polynuclear aromatic molecules that physically coat catalytic surfaces. Physical loss of activity also occurs as coke accumulates, ultimately partially or completely blocking catalyst pores as in supported metal catalysts.

Known promoters of coking, sooting and carsul formation include:

- Olefins potentially from refinery gas as fuel or poor quality hydrogen makeup
- Refinery hydrogen (e.g. Reformer) containing aromatics/BTEX as well as chlorides
- Acid Gas Enrichment feed streams containing BTEX

Another form of sooting is the deposition of carbon within the catalyst pores from disproportionation of carbon monoxide:



This mechanism effectively blocks the metal sites and reduces activity This is driven by active metal sites; hydrogen and water vapor inhibit the path, although hydrogen partial pressure is quite low in TGU conditions.

At TGU conditions this proceeds slowly. As CO is reduced considerably in concentration through the bed the occurrence is mostly in upper portion of the bed, advancing as catalyst is poisoned and reactive front moves down into the bed.

Cobalt is a commonly used ingredient in Fischer-Tropsch synthesis catalysts. However, formation rates are extremely low at the low partial pressures in a TGU application. , Nevertheless, diesel-ranged boiling hydrocarbons have been measured in TGU amine systems.

## Sooting

Sooting most commonly occurs when sub- or near-stoichiometric natural gas firing is used on startups and shutdowns, or by improperly operating inline reheat burners. Fine soot particles accumulate on the surface of catalyst particles and fill interstitial areas, restricting diffusion from the bulk to the catalyst interior and increasing pressure drop through the bed. At the extreme, soot particles can block macropores and restrict access to mesopores and micropores. This type of deactivation typically occurs at the top (or inlet) of the catalyst bed and can create a rigid crusty structure. It causes not only loss in catalyst performance, but also increases pressure drop through the converter vessel, thus lowering hydraulic capacity,

## Reaction to Produce Inactive Phases

Dispersed metals, metal oxides, metal sulfides, and metal carbides are typical catalytic phases, the surfaces of which are similar in composition to the bulk phases. If, one of these metal catalysts is oxidized, sulfided, or carbided, it will lose essentially all of its activity. These chemical modifications are closely related to poisoning, although the distinction is that rather than losing activity owing to the presence of an adsorbed species, the loss of activity is due to the formation of a new phase altogether

Reaction of  $\text{SO}_3$  with  $\gamma\text{-Al}_2\text{O}_3$  to produce aluminum sulfate  $\text{Al}_2(\text{SO}_4)_3$  is a serious cause of deactivation of alumina-supported catalysts in several catalytic processes, leading to support breakdown and catalyst pore plugging in several processes

Metal loss through formation of volatile compounds, e.g., metal carbonyls, oxides, sulfides, and halides in  $\text{CO}$ ,  $\text{O}_2$ ,  $\text{H}_2\text{S}$ , and halogen-containing environments, can be significant over a wide range of conditions, including relatively mild conditions. Carbonyls are formed at relatively low temperatures but high pressures of  $\text{CO}$ ; halides can be formed at relatively low temperatures and low concentration of the halogens. However, the conditions under which volatile oxides are formed vary considerably with the metal.

Reaction of  $\text{SO}_3$  with the alumina support to form aluminum sulfate can lead to support breakdown and catalyst pore plugging, oxidation of Co metal supported on alumina or silica to Co surface aluminates or silicates during high water partial pressure. Formation of  $\text{NiAl}_2\text{O}_4$  during reaction and steam regeneration of  $\text{Ni}/\text{Al}_2\text{O}_3$  in a slightly oxidizing atmosphere above about  $500^\circ\text{C}$  is also a possibility, especially if more reactive aluminas, e.g.,  $\gamma$ ,  $\delta$ , or  $\theta$  forms, are used as supports. Because reaction of  $\text{SO}_3$  with  $\gamma\text{-Al}_2\text{O}_3$  to produce  $\text{Al}_2(\text{SO}_4)_3$  is a serious cause of deactivation of alumina-supported catalysts in several catalytic processes (e.g., diesel exhaust abatement and SCR),  $\text{TiO}_2$  or  $\text{SiO}_2$  carriers are used rather than  $\text{Al}_2\text{O}_3$  or in the diesel or automotive exhaust the alumina catalyst is stabilized by addition of  $\text{BaO}$ ,  $\text{SrO}$ , or  $\text{ZrO}_2$ .

## Summary of Deactivation Mechanisms

Poisoning and thermal degradation are generally slow processes, while fouling and some forms of chemical and mechanical degradation can lead to rapid, catastrophic catalyst failure. Some forms of poisoning and many forms of fouling are reversible; hence, reversibly poisoned or fouled catalysts can be regenerated, though this is seldom practiced for TGU catalysts. On the other hand, chemical, mechanical, and thermal forms of catalyst degradation are rarely reversible.

It is often easier to prevent rather than cure catalyst deactivation. Some poisons and foulants can be removed from feeds using guard beds, scrubbers, and/or filters. Fouling, thermal degradation, and chemical degradation can be minimized through careful control of process conditions, e.g.,



effective destruction of ammonia in the SRU, avoiding feeds with BTEX to the SRU or TGU, avoiding reformer hydrogen as make-up (BTEX + Cl), utilizing natural gas instead of refinery gas for burner fuel ( $O_2$  slip, soot, olefins and heavy hydrocarbons, temperature excursions from changing stoichiometry) and avoiding  $SO_3$  formation in SRU. Effective control of air/oxygen to maintain tail gas  $H_2S:SO_2$  ratio with some benefit for control at elevated 4-6:1  $H_2S:SO_2$  ratio. Avoiding  $SO_2$  breakthrough or operation without hydrogen (coking) are vital.

Mechanical degradation can be minimized by careful control of heat-up rates and minimizing thermal cycles. Proper catalyst handling during loading, avoiding mechanical shock from high velocity impact, is important to prevent breakage and attrition. Catalyst design addresses choice of carrier materials, impregnation techniques, and/or catalyst particle forming methods and calcining.