University of Alberta

Optimal Selection of Delayed Coke Drum Materials Based on ASME Section II Material Property Data

by

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of

Master of Science

Mechanical Engineering

Spring 2013
Edmonton, Alberta

Your file Votre référence
ISBN: 978-0-494-96404-0

Our file Notre référence
ISBN: 978-0-494-96404-0

ABSTRACT

A remarkable contribution to the oil refining process has been made by introducing delayed coking process. The delayed coking enabled thermal cracking of heavy oil residue into useful lighter oil products and coke as a useful by-product. The achievement of the delayed coking has been made at the expense of increasing oil processing temperatures. Because the process is cyclic, the high cyclic operating temperatures combined with cyclic mechanical loads significantly reduce the operating life of the delayed coke drums. The objective of this thesis is to assess alternative materials for the delayed coke drum applications based on material property data provided in ASME Boiler & Pressure Vessel Code, Section II. The materials were compared based on their metallurgical and mechanical properties and the stress level in the coke drum shell obtained from finite element simulations for two critical operating scenarios, i.e. heating up stage and quenching stage. Among the materials studied, SA-302-C as a base material cladded with the nickel alloy N06625 is a proposed material pair for the delayed coke drum application.

ACKNOWLEDGEMENTS

I would like to express my appreciation to my supervisor Dr. Zihui Xia for his guidance, patience and support throughout this endeavor. I highly admire Dr. Xia's research enthusiasm, long teaching and research experience and exceptional knowledge.

I would also like to express my thanks to Dr. Pierre Mertiny, Dr. Feng Ju, Dr. Yejian Jiang, John Aumuller, Jie Chen, Yanxiang Zhang and the other members of the Advanced Composite Material Engineering group for their support and great discussions.

I am very grateful to my parents, my brother and my sister for their support and encouragement throughout this study.

I am especially thankful to my wife, Jelena Nikic, for being patient and supportive throughout this endeavor.

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CHAPTER 1 INTRODUCTION

1. 1 Introduction to Delayed Coking Process and Coke Drums

Sawarkar et al. [1] highlighted the importance of delayed coking process using the expression "zero resid refinery" for a refinery using delayed coking process because this process doesn't leave liquid bottom by-products that require tankage, but instead the delayed coking produces coke as a solid by-product that is finding its uses in different industries.

The delayed coke drum process is achieved by heating up heavy oil residue to higher temperatures than the temperatures of the other oil refining processes preceding the delayed coking. The high temperature and mechanical loads create severe loading conditions for the pressure vessels commonly called coke drums operating in delayed coking process. A delayed coking cycle as described by Penso et al. [2] consists of the following stages: A coke drum is initially preheated by steam. This stage is followed by pressure testing to reveal if any leaks of steam exist. Then a heavy oil residue preheated to about 482 °C is directed into the empty coke drum where with the filling stage the internal pressure is raised. The operating pressure is usually in a range from 100 to 500 KPa. Upon the completion of the heavy oil residue filling the cooling is started with steam and followed by quenching water from the bottom of the coke drum. After the cooling is finished the water is drained and the coke is cut and dumped out from the coke drum.

Therefore, the coke drums have to sustain the cyclic thermo-mechanical loads. Such loading condition may introduce different type of damages and reduce the operating life of the coke drums.

1. 2 History of Delayed Coke Drum Material Selection

High demand for oil and gas has significantly affected delayed coking operations as well coke drum design. Since inception of the delayed coking, coke drums have been evolving in size and the delayed coking cycle time has been decreasing. Sawarkar et al. [1] reported that before 1940's the coke drum diameter was 3 meters with the height of 12.2 meters while in 1999 the size of the coke drums were about tripled with the diameter of 8.5 meters and the height of 36.6 meters. At the same time, the cycle time was shortened from about 24 hours at the inception of the delayed coking to about 12 hours in the late Nineties. The evolvement of larger coke drums increased heavy oil processing volumes and consequently increased production losses during the maintenance shutdowns. Therefore, it is important for the oil refining industry to improve the reliability of coke drums. The oil refining industry can achieve the improvements through better design, better material selection and adjusting the operating conditions.

1996 API Coke Drum Survey Report [3] indicates that the base materials used for the shell of coke drums are Carbon steel and C - ½ Mo mainly used in early coke drums, and Chrome-Molybdenum steels (1 Cr, 1 ¼ Cr and 2 ¼ Cr) mainly used in newer coke drums with the trend towards selection of base steels with higher Chrome and Molybdenum contents. For the cladding material, the survey [3] indicates the use of stainless steel types 405, 410 and 410S, where the trend is towards increasing use of 410S.

Recent research by Xia et al. [4] has shown that the stress in the cladding of the coke drum shell exceeds the yield strength of the cladding material because of a larger mismatch of the coefficients of thermal expansion (CTE's) between the clad and base materials and a small thickness of the clad comparing to the thickness of the base. Ju et al. [5] additionally analyzed the behavior of the clad in the elastic-plastic range using a Finite Element Analysis (FEA) model of SA-387-22 base steel paired with 410S stainless steel clad. They concluded that under combined thermo-mechanical loading the clad will experience plastic shakedown.

Therefore, the recent findings by Xia et al. [4] and Ju et al. [5] suggest that the improvement in the reliability of the delayed coke drums can be accomplished by selecting better coke drum materials. This thesis extends on the research done by Xia et al. [4] and Ju et al. [5] with the material selection being the scope of this thesis.

1.3 Thesis outline

This thesis consists of six chapters. After the current introductory chapter, the second chapter is a literature review of the delayed coke drum research. The objectives of the thesis become clearer after the literature review; hence, the objectives of the thesis are stated at the end of the second chapter rather than at the end of the first introductory chapter. The third chapter presents the material selection based on mechanical and metallurgical properties. The fourth chapter shows FEA model set up and the results of the axisymmetric elastic-plastic analyses that use two different loading scenarios, one is only heating up stage with in-phase pressure and the other is a two-cycle loading scenario that includes the heating up and cooling down stages. The elastic-plastic FEA model in the fourth chapter compares materials based on the ratios of the maximum von Mises stress to yield strength of the materials studied during heating up stage. In addition, the fourth chapter compares the axial and hoop stress ranges in the clad of the coke drum shell for different base and clad material pairs during two heating up and cooling down cycles. The elastic-plastic model explores the differences in the stress caused by mismatch of the CTE's between the clad and base materials. The fifth chapter presents the model set-up and the results of the axisymmetric thermo-elastic FE analysis and comparison of materials based on the ratios of maximum von Mises stress experienced to yield strength of the materials as well comparison of stress ranges during water quenching stage. The fifth chapter also examines the influence of the thermal diffusivity and Young's modulus on the stress in the base materials. The last chapter presents the discussion of the research results and concludes this thesis

CHAPTER 2 LITERATURE REVIEW AND THE OBJECTIVES OF THE THESIS

2. 1 Introduction

Due to the large size of delayed coke drums and their large volume processing capability the loss of the production with the maintenance shutdowns of the coke drums generates high economical losses. Therefore, the reliability of coke drums has become the topic of interest for the oil refining industry and researchers. Extensive research has already been done analytically, experimentally or by field investigations.

This chapter will present a literature review that highlights the common problems in delayed coke drums as well the damage mechanisms. Knowing the problems and the damage mechanisms the thesis objectives will be stated at the end of this chapter.

2. 2 Literature Review

2. 2. 1 Common Coke Drum Problems

The severe loading condition in delayed coke drums in the form of combined thermal and mechanical loads may cause different types of damages. Figure 2-1 shows a simplified sketch of a delayed coke drum highlighting the most important features that will be used as a visual guide for understanding of common coke drum problems. The figure shows that a coke drum is supported by a skirt attached to the upper level of conical section by a weld. The plates are joined by circumferential and axial welds. Detail of the circumferential weld is also shown in the figure. The shell consists of a base metal that is cladded with a thin corrosion resistant clad. It should be noted that the weld is also overlaid with a corrosion resistant weld overlay as shown in Figure 2-1.

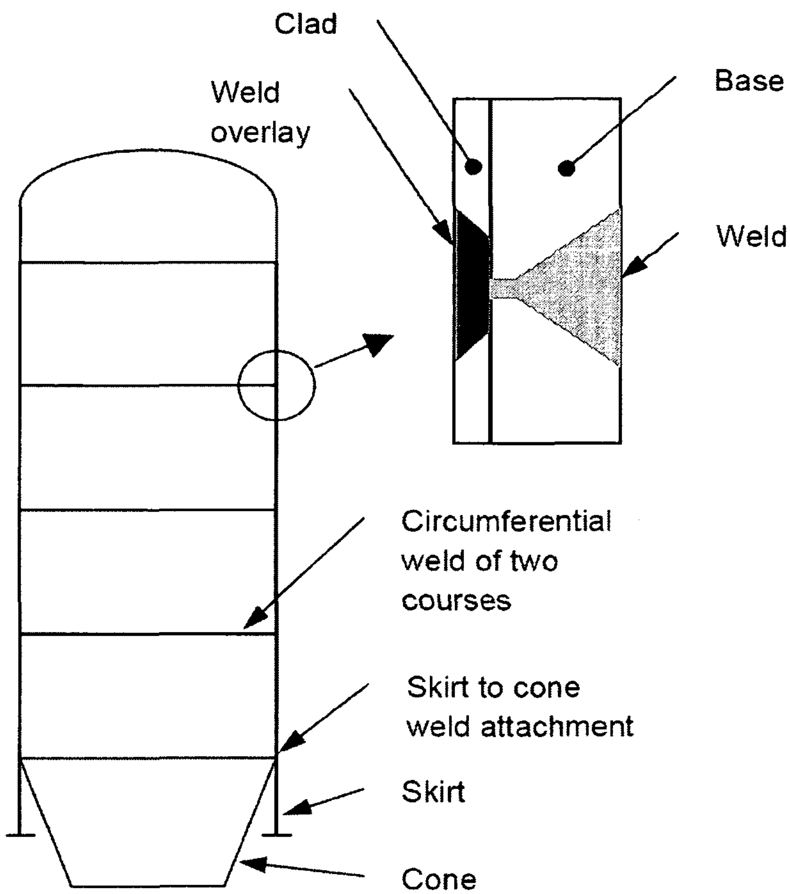

Figure 2-1: A Simplified Sketch of a Delayed Coke Drum

Per 1996 API Coke Drum Survey Report [3] the base materials used for the shell of coke drums are Carbon steel, C - ½ Mo and Chrome-Molybdenum steels (1 Cr, 1 ¼ Cr and 2 ¼ Cr), while for the cladding material stainless steel types 405, 410 and 410S are used. In addition, the Survey Report [3] indicates that for the weld overlay that joins clad plates, nickel based weld filler materials have been used since 1960's.

Ramos et al. [6] performed mechanical integrity evaluation of delayed coke drums indicating that the cracks mainly form in the clad, the welds that join shell courses and on the skirt to cone attachment welds. In addition, the authors [6] performed low fatigue tests of 1Cr – ½ Mo and 1 ¼ Cr - ½ Mo base metals and weld joints of these metals showing that the fatigue life was significantly decreased in welded joints in comparison to the base materials. Ramos et al. [7] further assessed coke drums using field measurements and FEA. Their findings from the field measurements indicated the existence of hot and cold regions random in location and the temperature difference that can cause high local strains/stresses responsible for bulging and cracking of the coke drum shell. Additionally, Ramos et al. [7] indicated that inspection records from coke drums show that cracking occurs less frequently as well as occurring randomly at the shell discontinuities before bulging of coke drum shell starts. The authors [7] identified that once bulges form on the coke drum shell, the fatigue rate increases and cracks start to form in the bulged areas.

Penso et al. [2] in a metallurgical study of delayed coke drum material samples identified different types of cracks occurring in the coke drums. The authors [2] indicated that the deepest cracks were found in the heat affected zones (HAZ) of internal welds, those cracks initiated close to the boundaries of high nickel alloys and stainless steel clad. Additionally, they identified the largest number of the cracks is in the stainless steel clad. The authors [2] also identified inter-bead surface cracks and inter-granular subsurface cracks in high nickel alloy weld overlays as well the base metal inclusion cracks in the HAZ.

Penso et al. [2] summarized some sources causing the cracking to be different. Types of corrosion, geometrical stress raisers as for instance weld toe geometries, high stresses caused by thermal cycling, local stresses caused by differences in CTE's at the interface of joining materials, the residual welding stresses, mismatch in tensile strength between weld and base metal, thermal shock on the internal surface of shell, as well the metallurgical effect of welding that creates a band of low strength material at the welding fusion boundaries. Another study by Penso et al. [8] indicated that cracking also occurs in bulged areas due to geometrical changes. They also identified cracking occurring in the weld attachments of the skirt and the cracks growing at external weld attachments.

Oka et al. [9] performed a field measurement on a coke drum using eight thermocouples placed in-line in vertical direction with a smaller spacing between the thermocouples in lower portion of the coke drum. The authors [9] showed that during the preheating and oil filling stage there is no significant variation in the temperature distribution, while during the quenching stage the temperature distribution is non-uniform and unpredictable, for example, even though the quenching water is injected from the bottom of the coke drum, in some instances the thermocouples that are at the higher location of coke drum recorded more rapid decrease in the temperature than the thermocouples at the lower locations recorded. The authors [9] performed FEA based on the data collected on a coke drum in field and concluded that the occurrence of hot and cold spots during quenching stage could cause high stresses resulted in permanent deformation or bulging of the coke drum shell.

The literature review of the research performed on coke drums [2, 6-9] clearly shows that the problems in the delayed coke drums mainly can be classified as bulging and cracking in the coke drum shells. In order to seek for a solution and to extend the operational life of coke drums it is important to understand the damage mechanisms that lead to the problems mentioned above.

2. 2. 2 Damage Mechanism

As indicated by Ramos et al. [7] and Penso et al. [2] most of the studies identified low cycle fatigue as dominant damage mechanism in delayed coke drums. Ramos et al. [7] studied the effect of initial quench flow rate on the damage of the coke drums based on field measurement data and concluded that the shell strain can be lowered by the decrease in the initial quench flow rate and consequently increase the fatigue life of coke drum shell. Xia et al. [4] indicated from the FEA results of a complete coke drum operating cycle that the temperature cycling causes severe and repeated bending of coke drum shell, in addition the authors [4] found that the stress in the clad exceeds the yield limit of the clad material due to a larger CTE difference between the clad and base materials and due to much smaller thickness of the clad than the thickness of the base. The findings of Ramos et al. [7] and Oka et al. [9] identified a random occurrence of the hot and cold spots during the quenching stage that intensify the stresses in the coke drum shell. Ju et al. [5] performed elastic-plastic finite element analysis on the entire coke drum structure as well as investigated the effects of local hot and cold spots on the coke drum shell. The authors [5] found that under in-phase cyclic thermal and pressure loading, which is close to the real loading scenario, the clad experiences plastic shakedown that implies low cycle fatigue as the main failure mode. The analysis also found that both clad and base material can yield under the attack of hot/cold spots. And repeating occurrence of hot/cold spots at same location can result in progressive bulging deformation. Chen [10] performed experimental study of coke drum materials for several different loading conditions similar to the loading scenarios of coke drums by using thin-walled tubular specimens. The type of the tests and the results of the study by Chen [10] are summarized as follows: One type of tests performed is strain controlled (±0.4%) or stress controlled (± 385 MPa) axial cyclic loading with constant internal pressure (7.446 MPa producing a hoop stress of 70 MPa) under two different constant temperatures (at ambient temperature and 427 °C). It was found that hoop ratcheting strains were accumulated causing bulging of the specimens. The ratcheting strains accumulated more at higher temperatures. The stress controlled axial cycling was more detrimental because tensile hoop strain and compressive axial strain could accumulate simultaneously. Another type of tests performed by Chen [10] is in-phase thermal-mechanical cyclic tests. They were run under either strain controlled (±0.4%) or stress controlled (± 400MPa) axial cycling with a constant internal pressure (7.446 MPa) with temperature cycling between 70 °C and 400 °C. This in phase loading case, as identified by Chen [10], could produce noticeable ratcheting strains by a small number of the thermo-mechanical cycles.

The above studies all point to the low cycle fatigue as a dominating damage mechanism in coke drums. This damage mechanism is characterized by the stresses that are experienced in each delayed coke drum operating cycle (bending stresses, and clad stress due to mismatch of CTEs) as indicated by Xia et al. [4]. These stresses further get intensified by the local stresses resulting from the occurrences of random hot and cold spots as indentified by Ramos et al. [7], Oka et al. [9] and Ju et al [5]. The stress caused by hot and cold spots can exceed the yield strength of both the base and clad materials [5], the experimental results obtained by Chen [10] show that in-phase thermo-mechanical cycling with the stresses or strains in plastic range can produce a noticeable accumulation of ratcheting strains (bulging) by a small number of cycles.

Due to high operating temperatures of delayed coke drums it is important to consider if creep is a potential damaging mechanism during coke drum operation. Church et al. [11] performed crack growth modeling and probabilistic life assessment of coke drums operating under fatigue conditions. The authors [11] pointed out that even though coke drums operate at peak temperatures that are within the creep range for low alloy steels the stresses associated with the operation are low, thus the authors [11] indicated that the potential for creep damage is low in the comparison to the thermal fatigue damage. There is some research done with regard to creep-fatigue interaction. Panwala et al. [12] performed creep-fatigue interaction study in coke drum skirt using API 579-1 approach and FEA, assuming ¼ Cr – ½ Mo low alloy steel and maximum temperature of 495 °C. They found that the most critical location for fatigue is at slot tip of the skirt. Penso et al. [13] also performed thermo-mechanical fatigue life assessments to evaluate life of skirt to cone attachment weld. In the creep-fatigue crack initiation model the authors [13] performed two analyses, with and without considering creep, respectively at 800 °F (427 °C). The results showed that there is no significant difference, however, the authors [13] pointed out that at higher temperatures this wouldn't be true.

From the literature review above it may be concluded that main failure modes in coke drums are bulging and different forms of cracking, while the main damage mechanism is low cycle fatigue attributed to severe thermo-mechanical cyclic loading during delayed coking process. In addition, it was possible to see from the literature review that there are different factors affecting the fatigue life of coke drum shell, thus there are several areas where improvements may be explored to increase the reliability of delayed coke drums. In particular, this study is a continuation on the research performed by Xia et al. [4] and Ju et al. [5] whose research results showed that high stress in the clad of coke drums is the consequence of the larger difference in CTE's between the base and cladding materials. Thus, a better material selection may contribute to the improvement of the reliability of coke drums.

2. 3 Thesis Objectives

The objective of this study is to explore alternative clad and base material combinations and select optimal clad and base pair for delayed coke drum applications.

To reach this objective the following is required:

- To select materials that will respond in lower stress at coke drum operating conditions.
- The material selection range should be within ASME Boiler & Pressure Vessel Code approved materials.
- The comparison of materials should be based on material data properties provided in ASME Boiler & Pressure Vessel Code, Section II [14].
- Among ASME approved materials only ductile materials should be considered in the selection such that a catastrophic failure is avoided in delayed coke drum service.

Other properties to be considered during the material selection are:

- Coefficients of thermal expansion.
- Mechanical properties.
- Metallurgical properties.

This study is mainly based on theoretical and numerical methods.

It is recommended that the results of this study are further verified experimentally. This task is currently carrying on in Professor Xia's research laboratory.

CHAPTER 3 COMPARISON OF MATERIALS BASED ON THERMO- MECHANICAL AND METALLURGICAL PROPERTIES

3. 1 Introduction

This chapter compares materials suitable for coke drum applications based on their thermo-mechanical and metallurgical properties. As indicated by Xia et al. [4] and Ju et al. [5], the high stress in the cladding exceeding the yield strength of the cladding material is caused by a greater mismatch in the CTE's of the clad and base materials and a very small thickness of the clad compared to that of the base.

Therefore, based on the result obtained by Xia et al. [4] and Ju et al. [5] the selection of the delayed coke drum materials in this study starts by matching the CTE's of the cladding and the base materials. However, in order to find optimal materials for delayed coke drum applications it is important to consider other material properties such as the properties relating to the heat transfer, mechanical and metallurgical properties. The goal of this study is to find materials with the properties that exceed the material properties of previously and currently used coke drum materials. If the goal is not achievable with some material properties, the intention is that those material properties are not to be significantly worse than those of the already used coke drum materials. The material selection is restricted to the materials approved by ASME Boiler & Pressure Vessel Code. In addition, among the ASME approved materials the selection of the materials is restricted to ductile, low alloy steels, for coke drum base material such that brittle (catastrophic) failure in the coke drums is avoided.

3. 2 Comparison of Materials Based on Thermo-Mechanical Material Properties

3. 2. 1 Matching CTE's of Clad and Base Materials

1996 API Coke Drum Survey Report [3] indicates the use of stainless steel types 405, 410 and 410S, where the trend is towards increased use of 410S as the cladding material for delayed coke drums. Based on ASME Section II [14] material property data, the CTE's of 405, 410 and 410S stainless steels are noticeably lower than those of commonly used coke drum base steels. The high stresses in the clad exceeding its yield strength during heating of coke drum shell are a consequence of a noticeable difference in the CTE's of the clad and base and a small thickness of the clad compared to the thickness of the base [4, 5].

In this study the precedence during the selection of the cladding materials is given to stainless steels, as less costly cladding option, than the high nickel alloys, provided that the functionality for delayed coke drum applications is achieved. Stainless steel type 405 belongs to the group of ferritic stainless steels [15], while 410 and 410S belong to the group of martensitic stainless steels [15]. ASME Section II [14] shows that there are other ferritic and martensitic stainless steels with higher chrome content while nickel is maintained at lower percentages, as such these stainless steels per ASME Section II [14] have even somewhat lower CTE's than those of types 405, 410 and 410S, which implies that the difference in CTE's between the clad and the base would be even greater than for the combinations that have already been used in coke drum applications.

If austenitic stainless steels are considered for the cladding application, based on the CTE data provided in ASME Section II [14], the austenitic stainless steels have higher CTE's compared to the CTE's of the coke drum base steels, thus also having mismatch in the CTE's between the base and clad. Additionally, McGuire [15] indicated that these stainless steels are less resistant to cyclic oxidation than ferritic due to the higher values of their CTE's that can cause spalling of the protective oxide layer, as well McGuire [15] pointed out that austenitic stainless steels may be prone to stress corrosion cracking. McGuire [15] additionally indicated that these stainless steels are prone to thermal fatigue due to their high CTE's and lower fatigue endurance limits.

CTE data of Duplex stainless steels provided in ASME Section II [14] shows that the CTE's of these stainless steels closely match the CTE's of coke drum base steels. However, ASME Section II [14] indicates that ASME Section VIII Division 1 doesn't permit use of the duplex stainless at the delayed coke drum operating temperatures (482 °C). These stainless steels can't be used in the service at the temperatures much greater than 300 °C since they form embrittling phases [15].

Hence, it can be concluded that a suitable cladding candidate for the coke drum shell cannot be found among stainless steels. Therefore, it is required to look for a functional solution among high nickel alloys. Nikic et al. [16, 17] selected high nickel alloys N06600 and N06625 indicating that these alloys paired with either currently used coke drum base steels or with a recommended new base steel candidate SA-302-C have significantly better matching of the CTE's. The improvement in the matching of the clad and base CTE's achieved by using new candidate materials compared to previously and currently used [1] material pairs is shown in Figure 3-1.

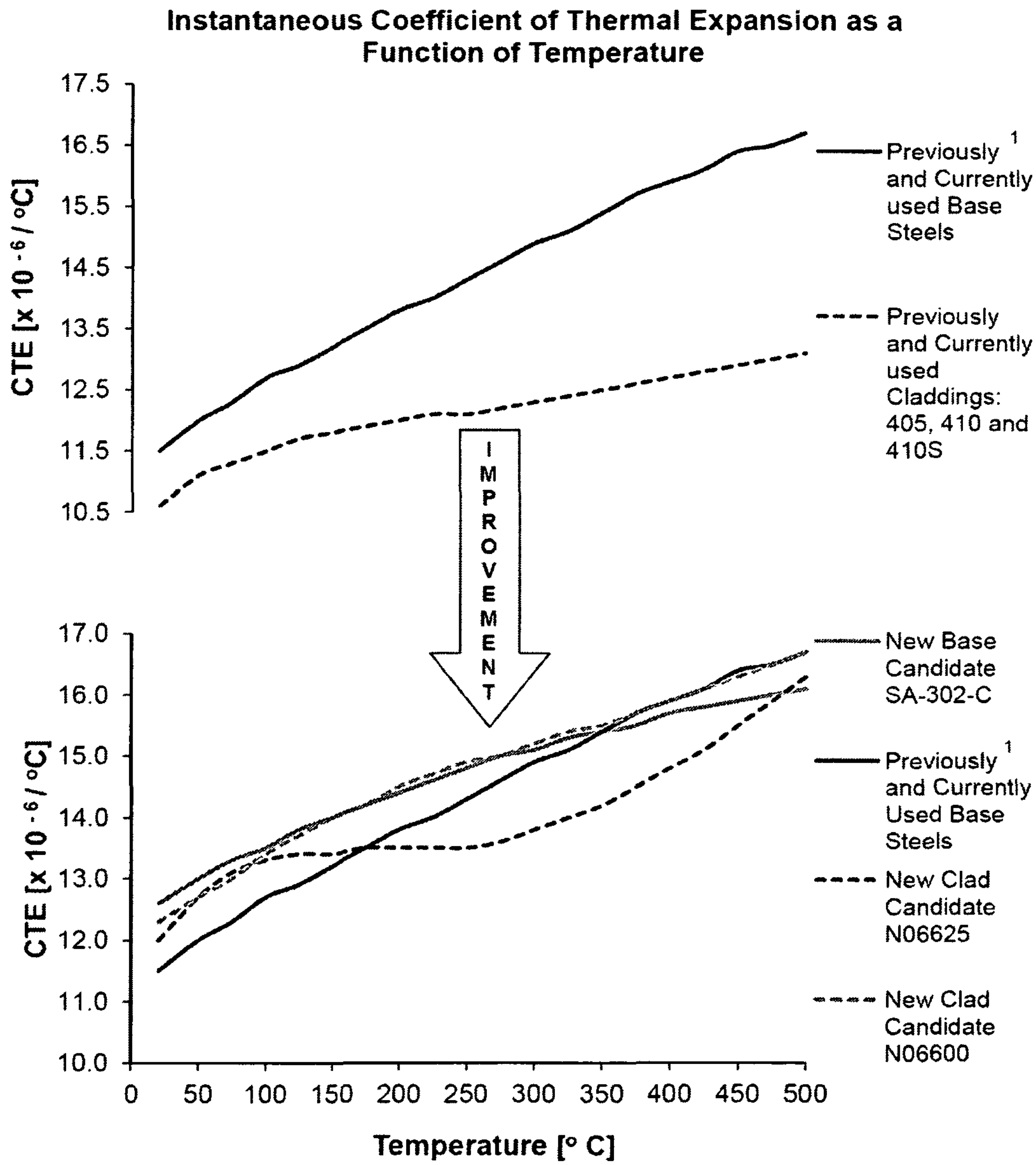

Figure 3-1: Improvement in matching of clad and base CTE's achieved by using new cladding candidates (Graph data per ref. [14])

[1] Previously and currently used base steels include SA516-70, SA-387 Grades 11, 12, 22 and SA-204-C.

3. 2. 2 Comparison of CTE's of Coke Drum Base Steels

Recalling Figure 3-1 it should be noted that already used coke drum base steels are represented with a single CTE graph curve. This is because ASME Section II [14] classifies materials in groups with the same CTE's. For instance, per ASME Section II [14] Group 1 materials have the same CTE value; this group includes carbon steel and majority of low alloy steels, as well all the previously and currently used coke drum base steels including SA516-70, SA-387 Grades 11, 12, 22 and SA-204-C. Per ASME Section II [14], SA-302-C belongs to the CTE Group 2 materials. What is important to note from Figure 3-1 that there is a small difference in the CTE's between already used coke drum base steels and SA-302-C. For a better comparison it is easier to see the difference if it is expressed in thermal strains for a temperature change from 20°C to 500°C. For this temperature range ASME Section II [14] indicates following thermal strains:

- Group 1 (Includes already used coke drum steels) = 6900 μ strain
- Group 2 (Includes SA-302-C) = 7100 μ strain

Therefore, the difference in the thermal strains in the temperature range from 20 °C to 500 °C is only 200 μ strain. Hence, it can be concluded that there is a small variation in the CTE's of the low alloy steels applicable for the delayed coke drum base. The small variation of CTE's of the low alloy steels applicable for delayed coke drum service should not have significance on the stress level. This will be verified later by ANSYS FE Analysis in chapters 4 and 5.

3. 2. 3 Comparison of Materials Based on Mechanical and Heat Conductivity Properties

As indicated in 1996 API Coke Drum Survey Report [3] the trend of selection of delayed coke drum base materials is towards steels with higher Chrome-Molybdenum contents. The properties of all already used coke drum steels and of new candidates are shown in Table 3-1 for better understanding of the industry trend in the selection of materials, and for the optimal selection in the current study.

It can be observed from the table that with the higher content of Chrome and Molybdenum the yield strength and the tensile strength increase while the ductility based on the percent elongation of 2 in (50 mm) specimen does not vary significantly; there is some improvement of the toughness visible in the trend of increase of Chrome and Molybdenum content in the base steels. Observing the new base steel candidate SA-302-C it can be noticed that it has the highest yield and the ultimate strength among the base steels considered and a similar percent of elongation as the other base steels.

When considering Young's modulus it can be seen that the higher the contents of Chrome-Molybdenum in the low alloy steels the higher Young's modulus. It should be noted that SA-204-C and SA-302-C have the lowest Young's modulus among the base steels in Table 3-1. Since the bending of the shell is caused by non-uniform temperature distribution during the quenching stage and the CTE's of the base steels are similar; thus, the shell may experience similar bending deformation. If the bending is approximately the same then the lower Young's modulus values may be beneficial in decreasing the stress level during the quenching stage. This will be further verified by FE analyses in chapter 5.

Comparing the properties of the cladding materials shown in the shaded region of Table 3-1 it can be seen that the new cladding candidates SB 168 N06600 Hot Rolled (HT) and SB 443 N06625 Grade 1 Annealed (ANN) have noticeably higher values of the yield and ultimate strength as well the percent elongation and somewhat higher Young's modulus values.

Considering the maximum applicable temperatures allowed by ASME Section VIII Division 1 [18], it can be seen that all the materials considered in this study meet the maximum coke drum operating temperature of 482°C. It should be noted that Chrome-Molybdenum base steels have higher application temperature (649°C) than SA-516-70, SA204-C and SA-302-C (538°C). This reflects on the values of maximum allowable stress at high temperatures. It should be noted that the values of maximum allowable stress at 500 °C are not proportional to the corresponding yield strengths since at this temperature, per ASME Section II [14], the maximum allowable stresses are determined based on the time dependant properties. It can be observed that Chrome-Molybdenum steels have higher values of the maximum allowable stress than that of SA-516-70, SA204-C and SA-302-C. However, it can be noted that the maximum allowable stress of SA-302-C (68.4 MPa) is comparable in value to that of SA204-C (67.2 MPa) which has already been used in the delayed coke drum service.

Table 3-1: Comparison of Coke Drum Base and Cladding Candidates (Data per Refs. [14, 18])

MATERIAL	NOMINAL COMPOSITION	MIN YIELD STRENGTH [MPa]		MIN TENSILE STRENGTH [MPa]		YOUNG'S MODULUS [GPa]		MIN % EL. IN 2 [in] OR 50 [mm]	MAX TEMP. [°C] APPLICATION LIMIT FOR ASME SEC VIII DIV 1	MAX ALLOW. STRESS [MPa]		IMPACT TEST EXEMPT. TEMP. [2] [°C]	THERMAL CONDUCTIVITY [W/m°C]		THERMAL DIFUSIVITY x 10^{-6}[m^2/s]	
		25 [°C]	500 [°C]	25 [°C]	500 [°C]	25 [°C]	500 [°C]			20 [°C]	500 [°C]		20 [°C]	500 [°C]	20 [°C]	500 [°C]
PREVIOUSLY AND CURRENTLY USED COKE DRUM MATERIALS																
SA 516 70	CARBON STEEL	262	162	483	332	202	151	21	538	138	33.6	-1 (AR)	60.4	40.5	18.1	7.92
SA 204 C	C-1/2 Mo	296	201	517	463	200	149	20	538	148	67.2	20 (AR)	41	34.8	11.87	6.77
SA 387 12 CL 2	1 Cr - 1/2 Mo	276	184	448	407	204	169	22	649	128	94.4	20 (ANN)	41	34.8	11.87	6.77
SA 387 11 CL 2	1 1/4 Cr-1/2 Mo-Si	310	206	517	464	204	169	22	649	148	72.9	20 (ANN)	41	34.8	11.87	6.77
SA 387 22 CL 2	2 1/4 Cr-1 Mo	310	218	517	421	210	175	18	649	148	89.4	20 (ANN)	36.3	33.7	10.53	6.62
SA 240 TP 405	13 Cr-1Al	172	111	414	290	201	157	20	538	115	67.3		24.6	25.4	7.12	4.84
SA 240 TP 410	13 Cr	207	134	448	314	201	157	20	649	128	69.2		24.6	25.4	7.12	4.84
SA 240 TP 410 S	13 Cr	207	134	414	290	201	157	22	649	118	69.7		24.6	25.4	7.12	4.84
NEW COKE DRUM MATERIAL CANDIDATES																
SA 302 C	Mn-1/2 Mo-1/2 Ni	345	229	552	482	200	149	20	538	158	68.4	-19 (AR)	41	34.8	11.87	6.77
SB 168 N06600 HR	72 Ni-15 Cr-8 Fe	241	201	586	586	213	186	30	649	161	134		14.9	22.1	3.97	4.83
SB 443 N06625 Gr 1 ANN	60Ni -22Cr -9Mo-3.5Cb	379	306	758	672	207	180	30	649	217	192		9.8	16.9	2.85	3.86

[2] Values per ASME Sec VIII, Div 1[18] impact test exemption temperatures are based on 25.4 mm plate thickness and either as-rolled (AR) or annealed (ANN) plate condition

Additionally, the literature review has shown that creep is of less concern as the damage mechanism in comparison to the low cycle fatigue; hence, in the analyses in the following chapters the yield strength will be used as a major failure related parameter during FE analyses. In addition, the impact test exemption temperatures allowed per ASME Section VIII Division 1 are listed in Table 3-1. This is a minimum design metal temperature in safe ductile range and the steels are compared based on as-rolled or annealed condition. It can be seen that SA-302-C has the lowest temperature exempt from impact test. Since this temperature is above transition temperature range from ductile to brittle it is a good indication that this steel has also lower transition temperature than the other steels in this study. Viswanathan [19] indicated that when comparing a class of materials with comparable strength the material with lower transition temperature usually has greater fracture resistance than that of the material with higher transition temperature. Considering the thermal conductivity and diffusivity properties it can be seen that from the base metal these properties are the highest for carbon steel (SA-516-70), SA387- 22 has the lowest value, while the other base materials including the new candidate material SA-302-C, have the same properties as shown in Table 3-1. Comparing the cladding materials it can be seen that the new candidates have significantly lower thermal conductivity and diffusivity properties as shown in Table 3-1.

Therefore, based on the comparison of the mechanical properties it was shown that new candidate materials generally have better mechanical properties than those previously or currently used coke drum materials. For the influence of

Young's modulus and the properties relating to the heat transfer in the shell further FE analysis is required which will be further discussed in chapter. 5. The following section will examine some metallurgical aspects of coke drum materials.

3. 3 Metallurgical Properties of Delayed Coke Drum Material Candidates

3. 3. 1 Corrosion Resistance of Cladding Materials

The cladding has the main role to protect the base steel against corrosion. Per 1996 API Coke Drum Survey Report [3] stainless steel types 405, 410 and 410S, are used as cladding material where the trend is towards increased use of 410S type. It is necessary to examine the applicability of high nickel alloys N06600 and N06625 for the cladding from the aspect of their corrosion resistance. Kalpakjian [20] indicates that the minimum chrome content in stainless steels required for passivation to occur is 10-12 % weight. Table 3-2 compares the cladding alloys contents based on the data from ASME Section II [14]. It can be seen from Table 3-2 that the cladding candidate materials, N06600 and N06625 are characterized by higher content of Chrome and very high content of Nickel, as such these alloys in general can provide better corrosion resistance. Handbook of Corrosion Data [21] indicates that Nickel based alloys in general poses extremely effective corrosion resistance in service environments ranging from subzero to high temperature, but the Handbook [21] indicates that at the temperatures above 315-371 °C in sulfur containing environments these alloys are prone to general and intercrystalline corrosion caused by sulfur containing compounds.

Table 3-2: Chemistry of Cladding Materials (Data per Ref [14])

MATERIAL	SA 240 TP 405	SA 240 TP 410	SA 240 TP 410S	SB 168 N06600 HT	SB 443 N06625 Gr 1 ANN
NOMINAL COMPOSITION	12 Cr-Al	13 Cr	13 Cr	72 Ni-15 Cr-8 Fe	60Ni -22Cr -9Mo-3.5Cb
Alloying Element	%	%	%	%	%
C	0.08	0.08–0.15	0.08	0.15 max	0.10 max
Mn	1	1	1	1.0 max	0.50 max
Cr	11.5–14.5	11.5–13.5	11.5–13.5	14.0–17.0	20.0 min 23.0 max
Mo					8.0 min 10.0 max
P	0.04	0.04	0.04		0.015 max
S	0.03	0.03	0.03	0.015 max	0.015 max
Si	1	1		0.5 max	0.50 max
Ni	0.6	0.75	0.6	72.0 min	58.0 min
Other	Al 0.10–0.30			Fe 6.0–10.0, Cu 0.5 max	Nb+Ta 3.15 min 4.15 max Co (if determined) 1.0 max Fe 5.0 max Al 0.40 max Ti 0.40 max

Even though in the delayed coking process the residue contains sulfur compounds and operating temperatures are above 371°C, White [22] indicates that high nickel filler metal, 65Ni-15Cr-Fe, is used in coke drums for clad restoration because the coke can protect the filler metal from accelerated sulfur attack. White [22] further pointed out that coke drums are the only high temperature pressure vessels which operate in sulfur containing environment where the high nickel alloy 65Ni-15Cr-Fe is normally used. In addition, 1996

API Coke Drum Survey Report [3] also indicated the use of nickel based weld filler materials for the weld overlay of the cladding plates in coke drums since 1960's. The survey [3] indicated that nickel based weld materials used for cladding repair were rated good or very good in respect of the corrosion resistance. Therefore, the successful use of the nickel based weld filler metals in coke drum services, as pointed out by Nikic et al. [16, 17], is what demonstrates that N06600 and N06625 are suitable cladding materials for corrosion protection of coke drum base steels.

3. 3. 2 Chemistry of Coke Drum Base Steels

It is important to compare the base steels based on their chemistry. In order to perform the comparison a literature review of individual elements and their influence on the properties of the steel has been completed and summarized below:

- Carbon – improves hardenability, strength, hardness while reduces ductility and toughness and weldability [20]
- Manganese – improves hardenability and strength, combines with embrittling sulfur, reduces hot shortness and decreases weldability [20, 23]
- Chromium – improves toughness, hardenability, corrosion resistance, high temperature strength and wear [20]
- Molybdenum – improves hardenability, toughness, elevated temperature strength, improves creep resistance and reduces temper embrittlement [20]

- Phosphorus – improves strength and hardenability, machinability, significantly reduces ductility and toughness [20]
- Sulfur – improves machinability in combination with manganese, decreases impact strength and ductility [20]
- Silicon – improves strength hardness and corrosion resistance, and electrical conductivity, decreases machinability and cold forming ability, used primarily as deoxidizier [20, 23]
- Nickel – improves strength, toughness and hardenability, as well corrosion resistance, strong austenite stabilizer [20, 23]

Table 3-3 shows the chemistry of the coke drum base steels. It can be observed that the main difference is in the presence of Chromium, Nickel and level of Carbon and Manganese. In addition, SA-387-22 is characterized with higher level of Molybdenum. The comparison of mechanical properties earlier revealed that increase in the strength in the alloys with increasing content of Chrome-Molybdenum is followed with increase in Young's modulus. It was assumed that this may influence the stress level during the quenching stage as a consequence of thermal bending. As an alternative, SA-302-C is used with higher strength but lower Young's modulus. It can be seen from Table 3-3 that this material has similar composition as SA-204-C which has already been used in coke drum service. The difference is the presence of Nickel, slightly lower content of Carbon and higher content of Manganese. Based on the effects of alloying elements on the properties of steel listed above per references [20, 23] it can be seen that Nickel can be considered as a substitute for Chrome as a toughness improver, while the higher content of Manganese is beneficial to reduce hot shortness and tie sulfur as a embrittling element.

Table 3-3: Chemistry of Base Materials (Data per Ref [14])

MATERIAL	SA 516 70	SA 204 C	SA 387 12 Cl 2	SA 387 11 Cl 2	SA 387 22 Cl 2	SA 302 C
NOMINAL COMPOSITION	CARBON STEEL	C-1/2 Mo	1 Cr - 1/2 Mo	1 1/4 Cr-1/2 Mo-Si	2 1/4 Cr-1 Mo	Mn-1/2 Mo-1/2 Ni
Alloying Element	%	%	%	%	%	%
C	0.28	0.23	0.04-0.17	0.04-0.17	0.04-0.15	0.2
Mn	0.79-1.30	0.98	0.35-0.73	0.35-0.73	0.25-0.66	1.07-1.62
Cr			0.74-1.21	0.94-1.56	1.88-2.62	
Mo		0.41-0.64	0.40-0.65	0.40-0.70	0.85-1.15	0.41-0.64
P	0.035 max	0.035 max	0.035 max	0.035 max	0.035 max	0.035 max
S	0.035 max	0.035 max	0.035 max	0.035 max	0.035 max	0.035 max
Si	0.13-0.45	0.13-0.45	0.13-0.45	0.44-0.86	0.50 max	0.13-0.45
Ni						0.37-0.73

3. 3. 3 Embrittlement Phenomena of Coke Drum Base Steels

The operating temperatures of coke drums are high enough that the low alloy steels may experience different forms of embrittlement. ASME Section II [14] indicates that carbon steel, carbon manganese and carbon molybdenum steels are prone to graphitization, the phenomena where at high temperatures above 425°C graphite particles form. ASME Section II [14] further indicates that if the particles don't align along a plane this is not considered a problem but there is a tendency that the graphite particles align along heat affected zones or in cold worked regions, forming continuous planes that can fail catastrophically. Per ASME Section II [14] SA-516 70 is prone to graphitization above 425°C while SA-204-C and SA-302-C above 475°C. Chrome-Molybdenum steels are not prone to graphitization [14]

ASME Section II [14] indicates another type of embrittlement, called temper embrittlement characteristic for Ni-Cr, Ni, Cr-Mo and Cr-Mo steels when they are in service in the temperature range from 315°C to 595°C. This type of embrittlement is caused by segregation of impurities at grain boundaries and can be reduced by restricting the amounts of impurities [14].

Another phenomenon called creep embrittlement occurs at high temperatures resulting in loss of ductility and intergranular failure caused by impurities in steel where sulfur is most damaging. [24] The presence of manganese which is a strong sulfide former improves ductility of steel in creep [24].

Therefore, the literature review above implies that SA-302-C is susceptible to graphitization but with regard to this phenomenon it is comparable to already used base steel in coke drum service, SA-204-C. Additionally, with regard to temper embrittlement SA-302-C doesn't have any chrome in its chemical composition and as such does not belong to the group of the steels that are susceptible to temper embrittlement. Besides, SA-302-C has the highest content of manganese than that of the other base steels considered in this study, which is beneficial for prevention of creep embrittlement.

3. 3. 4 Weldability of Coke Drum Base Steels

Nikic et al. [16, 17] used ASME P Numbers and corresponding groups to compare materials' weldability and indicated that SA-302-C is more difficult to weld than SA-204-C but easier to weld than chrome steels. ASME Section IX [25] indicates that the material grouping assigns P-Numbers and Groups according to their comparable characteristics as composition, weldability etc. Table 3-4 shows the base metals in increasing order of P Numbers.

Table 3-4: P Numbers and Groups for Coke Drum Base Steels (Data per Ref [25])

MATERIAL	P NUMBER	GROUP
SA-516-70	1	2
SA-204-C	3	2
SA-302-C	3	3
SA-387-12 & 11	4	1
SA-387-22	5A	1

Per ASME Section VIII, Division 1 [18] Post Weld Heat Treatment (PWHT), normal holding temperature for P numbers 1 and 3 and Groups 1, 2 and 3 is 595°C. This temperature for P number 4, Groups 1 and 2 is 650°C, while it is 675°C for P number 5A, Group 1. Therefore, it can be seen that as the P Numbers increase for carbon and low alloy steel the PWHT holding temperature requirement increases. Higher PWHT requirements are good indicative of difficulty of material to weld, i.e. in the case of carbon and low alloy steels the higher P Number the more difficult material to weld. Therefore from Table 3-4 it can be seen that SA-302-C has lower P number than Chrome steels that have already been used in coke drum service, i.e. SA-302-C is easier to be weld than SA-387-11, 12 and 22 Chrome steels. Per ASME Section VIII, Division 1 [18], in some cases the PWHT may be exempted. Of particular interest here is P Number 3 Groups 2 and 3 to compare SA-204-C and SA-302-C. Per ASME Section VIII, Division 1 [18], PWHT is mandatory for P Number 3 Group 3, while for P Number 3 Group 2 PWHT is mandatory over 5/8 in (16 mm) nominal thickness. This indicates that SA-302-C is somewhat more difficult to weld than SA-204-C. This is reasonable since SA-302-C has higher content of Manganese which, beside its benefits, impairs weldability [20, 23]. Hence, it can be concluded that from the aspect of weldability and reparability SA-302-C is applicable candidate for coke drum base steel candidates.

3. 4 Summary

New delayed coke drum cladding candidates, N06600 and N06625, significantly better match CTE's of coke drum base steels than stainless steels currently used in coke drum service as cladding materials. In addition N06600 and N06625 are stronger materials with grater ductility; these materials also meet the corrosion requirements for coke drum applications.

New base candidate, SA-302-C, is a stronger material than the other materials considered in this study, in addition this material has similar ductility to other materials, as well it is also comparable with regard to embrittlement phenomena to other materials. With regard to weldability and reparability SA-302-C is better than Chrome steels used in delayed coke drum service. Beside its greater strength this material has low Young's modulus, which is assumed to be beneficial for coke drum application. This assumption is to be verified through FE analyses presented in the following chapters.

CHAPTER 4 AXISYMMETRIC ELASTIC-PLASTIC FINITE ELEMENT ANALYSIS [1,2]

4. 1 Introduction

To assess the stress level in the coke drum shell due to mismatch of the CTE's of the cladding and base materials an axisymmetric elastic-plastic FEA model was used. Materials were compared based on two different loading scenarios. One loading scenario was used to compare eleven base and clad material pairs based on the maximum von Mises stress to yield strength ratio during heating up stage with in-phase internal pressure. In addition, new candidate pair SA-302-C/N06625 and adopted industry pair SA-387-22/410S were compared based on axial and hoop stress ranges with a two cycle loading scenario which includes heating up and cooling down stages with in-phase internal pressure. ANSYS FEA software was used for the analyses.

The results show that a considerable achievement is made with better matching of the clad and base CTE's. Thus, N06600 and N06625 clad remained in the elastic range while 410S stainless steel yielded and plastically deformed. In addition, it was shown that as a result of plastic deformation of 410S stainless steel clad the axial and hoop stress range is significantly higher.

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[1] A version of a part of this chapter has been published. Nikic, M., Xia, Z., 2012, "Alternative Selections of Delayed Coke Drum Materials Based on ASME Material Property Data", *Proceedings of the ASME 2012 Pressure Vessels & Piping Division Conference PVP2012*, ASME PVP2012-78548

[2] A version of a part of this chapter has been submitted for review. Nikic, M., Xia, Z., Du Plessis, P., 2012, "Assessment of Coke Drum Materials Based on ASME Material Property Data", ASME J. Pressure Vessel Technology, PVT-12-1052 (ASME PVT Journal Paper Manuscript under Review)

4.2 Model Set-Up [3,4]

Elastic-plastic model has been established in the study performed by Ju, Aumuller, Xia and Du Plessis [5]. The study [5] examined the behavior of the clad above its yield point indicating that plastic shakedown in the clad occurs under combined mechanical and thermal loads. The same model established by Ju et al. [5] was used in this study. The model set-up is shown in Figure 4-2. For elastic-plastic analysis a bi-linear kinematic hardening rule was used. Temperature dependant material properties were used per ASME Section II [14]. The properties at six temperatures (20, 100, 200, 300, 400 and 500°C) were entered into FE model. ANSYS element PLANE 182 with axisymmetric option was used for the analysis. The size of a clad element used is 0.802 mm x 0.635 mm and the size a base element used is 0.802 mm x 0.762 mm. Thus, a very fine mesh was used to guarantee converged results are obtained.

The model set-up characteristics are as follows:

a) Dimensions of the coke drum shell course are:

- The inside radius = 3962.4 mm
- The course height = 76.2 mm
- The base thickness = 22.86 mm
- The clad thickness = 2.54 mm

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[3] A version of this section has been published. Nikic, M., Xia, Z., 2012, "Alternative Selections of Delayed Coke Drum Materials Based on ASME Material Property Data", *Proceedings of the ASME 2012 Pressure Vessels & Piping Division Conference PVP2012*, ASME PVP2012-78548

[4] A version of this section has been submitted for review. Nikic, M., Xia, Z., Du Plessis, P., 2012, "Assessment of Coke Drum Materials Based on ASME Material Property Data", ASME J. Pressure Vessel Technology, PVT-12-1052 (ASME PVT Journal Paper Manuscript under Review)

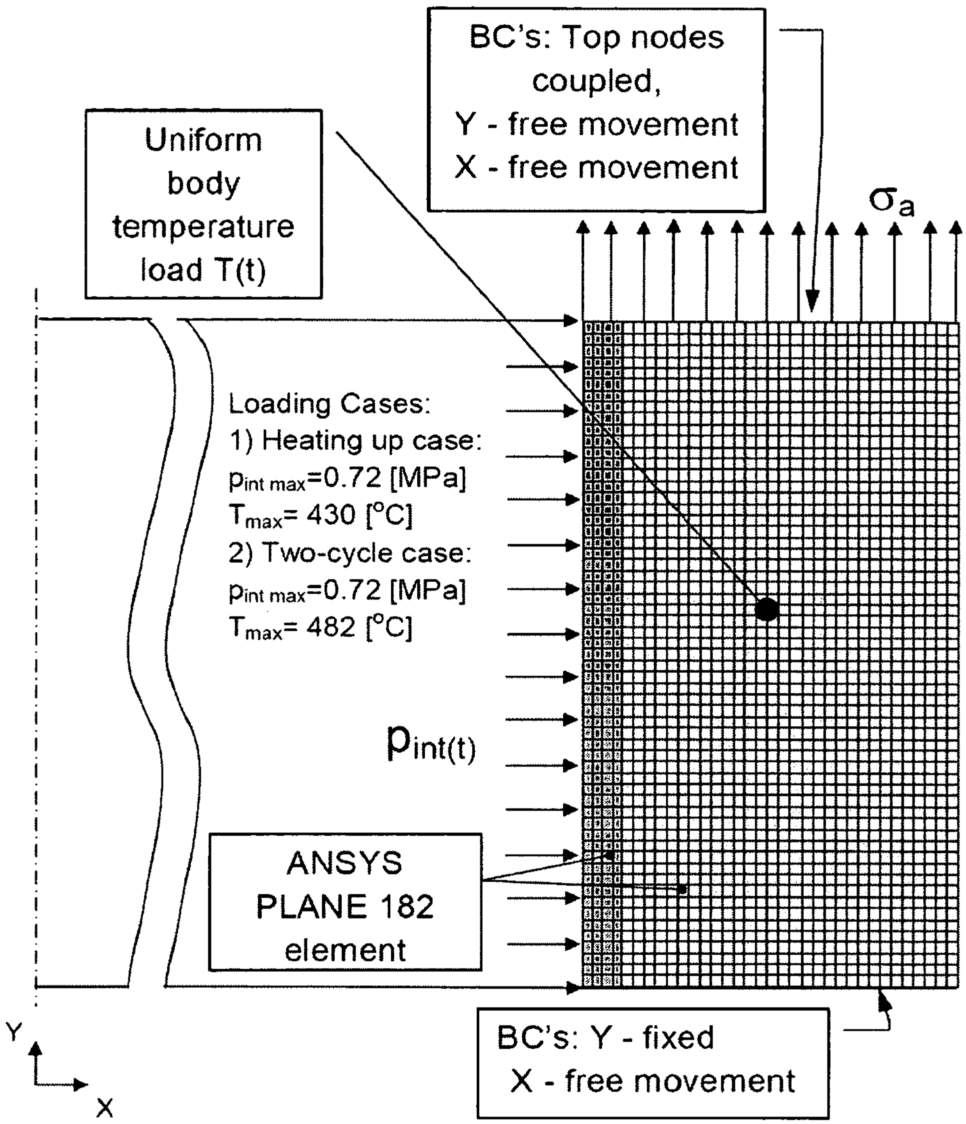

Figure 4-1: Axisymmetric Elastic-Plastic Finite Element Model (Adapted from Refs. [16, 17])

b) The model is constrained and loaded as follows:

- The bottom of the course is free to move in radial (X) direction and fixed in vertical (Y) direction.
- The top surface is free to move in both (X) and (Y) directions; however, the nodes are coupled in vertical (Y) direction, meaning that they move equally in (Y) direction such that the coupling creates "plane remains plane" constraint.

- The temperature is a function of time (T(t)) and it is applied as a uniform body load.
- The internal pressure ($p_{int}(t)$) is also a function of time and it is applied to the internal surface of the course in-phaselly with the body temperature, while the axial stress (σ_a) caused by the internal pressure is applied to the top surface in positive (Y) direction.
- The pressure and temperature are applied using two different loading scenarios:
  - Heating up case where the temperature and the pressure are applied in-phaselly until they reach their maximums of 430°C and 0.72 MPa respectively.
  - Two-cycle case where the pressure and temperature are applied in-phaselly in two heating and cooling cycles. The maximum temperature for this loading scenario is 482°C and maximum pressure is 0.72 MPa. For both cycles the maximum temperature and pressure are held for 4 seconds.

It should be noted that this model uses bilinear kinematic hardening rule, as such the model is rate-independent elastic-plastic model; however, for two cycle model the maximum loads are kept constant for 4 seconds since it is easier to observe that yielding starts before maximum loads are reached. The yield strength decreases with the increasing temperature. When the yielding starts the stress has the highest value, then the stress follows the yield strength and decreases together with the yield strength until the maximum temperature is reached. This will be shown graphically in section 4.4.

4. 3 Results of Elastic-Plastic Analysis for Heating up Loading Case [5, 6]

For this loading case the model was heated up from 25°C to 430°C with in-phaselly applied internal pressure from 0 MPa to 0.72 MPa. Eleven material pairs were compared based on the ratio of the maximum von Mises stress to yield strength as shown in Table 4-1. Von Mises stress is measured at the maximum temperature and pressure. Yield strength values at the maximum temperature are obtained from ASME Section II [14]. Von Mises stress to yield strength ratio is then calculated from the obtained values and expressed in percents. The materials that yield are shown in Table 4-1 with 100% Von Mises stress to yield strength ratio.

The following is observed from the results shown in Table 4-1:

- Both, the base and the cladding materials remain in the elastic range when any of the base materials studied is paired with either N06600 or N06625 high nickel alloy cladding materials. It should be noted that for these material combinations von Mises stresses are far below their yield strengths.

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[5] A version of this section has been published. Nikic, M., Xia, Z., 2012, "Alternative Selections of Delayed Coke Drum Materials Based on ASME Material Property Data", *Proceedings of the ASME 2012 Pressure Vessels & Piping Division Conference PVP2012*, ASME PVP2012-78548

[6] A version of this section has been submitted for review. Nikic, M., Xia, Z., Du Plessis, P., 2012, "Assessment of Coke Drum Materials Based on ASME Material Property Data", ASME J. Pressure Vessel Technology, PVT-12-1052 (ASME PVT Journal Paper Manuscript under Review)

Table 4-1: Results of Elastic-Plastic Analysis during Heating up Stage [16, 17] (Reprinted with Permission from ASME)

BASE/ CLAD PAIR	SA-387-12 Cl.2/N06600 SB-168 H.R.		SA-387-12 Cl.2/N06625 SB-443 Gr.1 ANN.	
	BASE	CLAD	BASE	CLAD
VON MISES STRESS [MPa] AT MAX. PRESSURE and TEMPERATURE	101	69	94	136
YIELD STRENGTH [MPa] AT MAXIMUM TEMPERATURE	196	211	196	311
VON MISES/ YIELD RATIO IN %	51.6	32.7	47.6	43.6
BASE/ CLAD PAIR	SA-387-11 Cl.2/N06600 SB-168 H.R.		SA-387-11 Cl.2/N06625 SB-443 Gr.1 ANN.	
	BASE	CLAD	BASE	CLAD
VON MISES STRESS [MPa] AT MAX. PRESSURE and TEMPERATURE	101	69	94	136
YIELD STRENGTH [MPa] AT MAXIMUM TEMPERATURE	223	211	223	311
VON MISES/ YIELD RATIO IN %	45.4	32.7	42.0	43.6
BASE/ CLAD PAIR	SA-387-22 Cl.2/N06600 SB-168 H.R.		SA-387-22 Cl.2/N06625 SB-443 Gr.1 ANN.	
	BASE	CLAD	BASE	CLAD
VON MISES STRESS [MPa] AT MAX. PRESSURE and TEMPERATURE	102	65	94	133
YIELD STRENGTH [MPa] AT MAXIMUM TEMPERATURE	236	211	236	311
VON MISES/ YIELD RATIO IN %	43.1	31.1	39.8	42.6
BASE/ CLAD PAIR	SA-204-C/N06600 SB-168 H.R.		SA-204-C/N06625 SB-443 Gr.1 ANN.	
	BASE	CLAD	BASE	CLAD
VON MISES STRESS [MPa] AT MAX. PRESSURE and TEMPERATURE	101	76	93	142
YIELD STRENGTH [MPa] AT MAXIMUM TEMPERATURE	211	211	220	311
VON MISES/ YIELD RATIO IN %	47.7	36.0	42.1	45.7
BASE/ CLAD PAIR	SA-302-C/N06600 SB-168 H.R.		SA-302-C/N06625 SB-443 Gr.1 ANN.	
	BASE	CLAD	BASE	CLAD
VON MISES STRESS [MPa] AT MAX. PRESSURE and TEMPERATURE	96	109	89	182
YIELD STRENGTH [MPa] AT MAXIMUM TEMPERATURE	265	211	265	311
VON MISES/ YIELD RATIO IN %	36.4	51.9	33.6	58.3
BASE/ CLAD PAIR	SA-387-22 Cl.2/410S			
	BASE		CLAD	
VON MISES STRESS [MPa] AT MAX. PRESSURE and TEMPERATURE	93		155	
YIELD STRENGTH [MPa] AT MAXIMUM TEMPERATURE	236		155	
VON MISES/ YIELD RATIO IN %	39.4		[2] 100	

[2] For combination of SA-387-22 and 410S the clad material starts yielding at temperature of 317 °C with pressure of 0.52 MPa before the temperature and pressure reach their maximum values. After the yielding the clad is undergoing more plastic deformation until the temperature and pressure reach their maximum values.

- Clad 410S stainless steel yields when combined with SA-387-22 base, the yielding of 410S occurs before the maximum temperature and pressure is reached at the temperature of 317 °C and pressure of 0.52 MPa.

- N06625 has higher von Mises stress than N06600 clad for any combination of the base steels. This is due to a greater mismatch of the CTE's between N06625 and base steels than the mismatch in the CTE's of N06600 and the base steels.
- N06625 has greater yield strength than N06600, as a result, high yield strength of N06625 maintains low ratio of von Mises stress to yield strength.
- The highest ratio of von Mises stress to yield strength in N06625 is 58.3% when N06625 is paired with SA-302-C base.
- The highest ratio of von Mises stress to yield strength in N06600 is 51.9% when N06600 is paired with SA-302-C base.
- The lowest ratio of von Mises stress to yield strength (33.6 %) is in the base SA-302-C when paired with N06625

It is important to note that even if clad 410S stainless steel was paired with any other base steels considered in this study the yielding of 410S clad would occur. This is expected as the CTE's of the base steels are similar, SA-204-C and SA-387 grades 11 and 12 have the same CTE's per ASME Section II [14] as SA-387-22 while SA-302-C has slightly higher CTE than the other base steels studied. The numerical results have confirmed the statement in section 3.2.2 that the small variation of CTE's of the low alloy steels applicable for delayed coke drum service should not have significance on the stress level.

4. 4 Results of a Two-Cycle Elastic Plastic Model

Two-cycle loading condition for the elastic-plastic model is shown in Figure 4-2. It should be noted that the maximum temperature for the cyclic analysis is 482°C, which is delayed coke drum operating temperature. The temperature is applied with in-phase pressure from 0-0.72 MPa. In the previous loading scenario, where only uniform heating was considered, the maximum temperature applied to the model was 430°C. The in-phase pressure for the uniform heating case was the same. Although in the previous loading scenario the temperature was 430 °C (below coke drum operating temperature of 482°C) the yielding occurred even before the maximum pressure and temperature were reached. Thus, for two-cycle loading scenario it is expected to see more plastic deformation because the maximum temperature is higher than that of the first loading case.

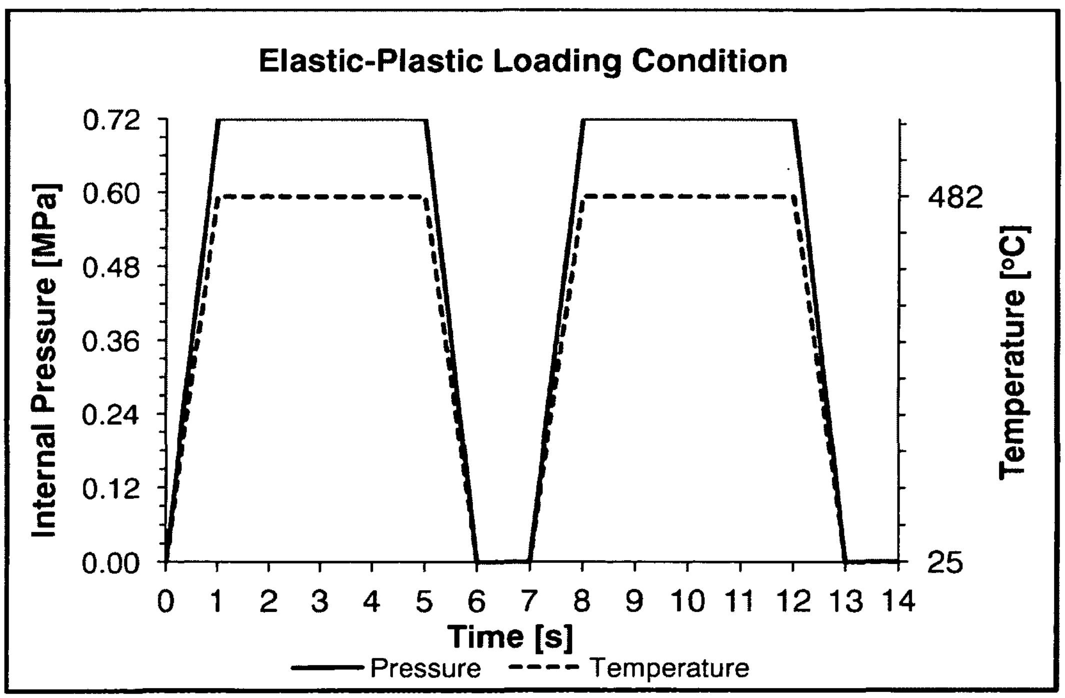

Figure 4-2: In-Phase Internal pressure and Temperature Loads of Elastic-Plastic Model

4. 4. 1 Von Mises Stress Results for Two-Cycle Loading Condition

This section compares the results of the industry adopted pair SA-387-22 /410S and a new candidate pair SA-302-C/ N06625. Figure 4-3 shows von Mises stress in the clad 410S. It can be observed from Figure 4-3 that yielding starts before the maximum temperature of 482°C and maximum internal pressure of 0.72 [MPa] are reached. After the yield strength is reached, the cladding plastically deforms until the maximum temperature and pressure are reached. It is important to note from Figure 4-3 that between 6 s and 7 s there is no load applied but von Mises stress is high. This is a residual stress as a consequence of the plastic deformation of 410S stainless steel clad during the heating up stage.

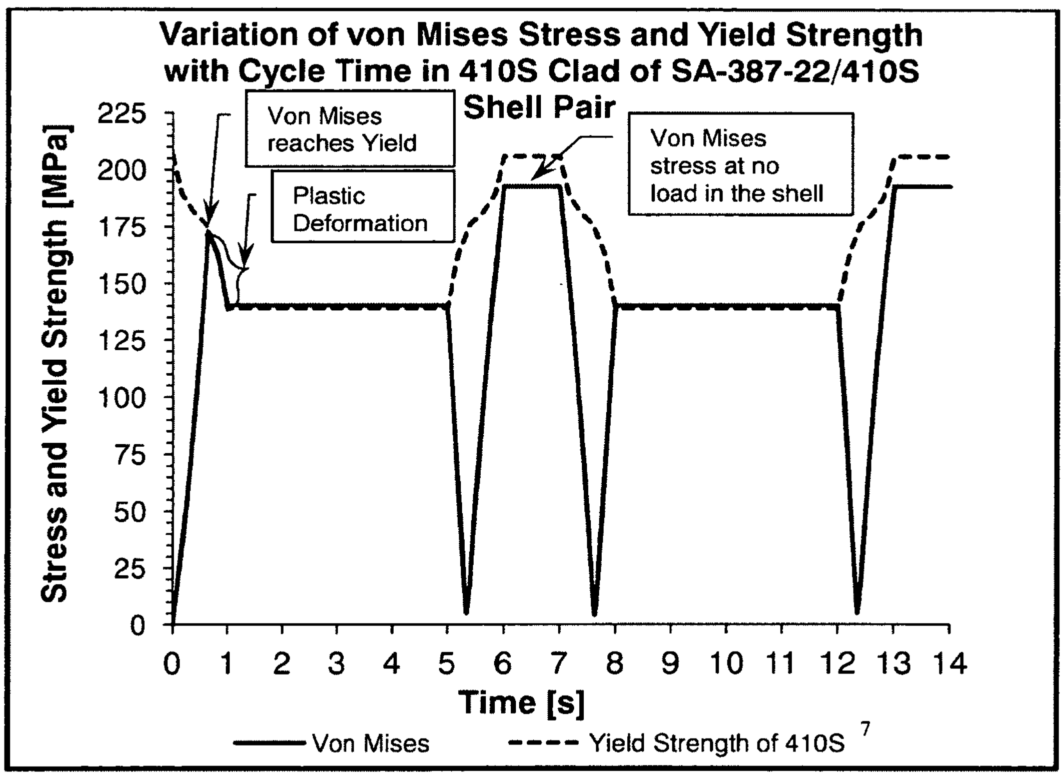

Figure 4-3: Variation of Von Mises Stress and Yield Strength with Cycle Time in the Clad of SA-387-22/410S Shell Pair

[7] Temperature Dependant Yield Strength data is per ASME Sec II [14]

When considering new base candidate material, SA-302-C paired with N06625 cladding, it can be seen from Figure 4-4 that von Mises stress is far below the yield strength; hence, the clad remains in the elastic range. Since there was no plastic deformation of the clad it can be observed that when there is no pressure and temperature loads applied (6-7 s) von Mises stress is 0.

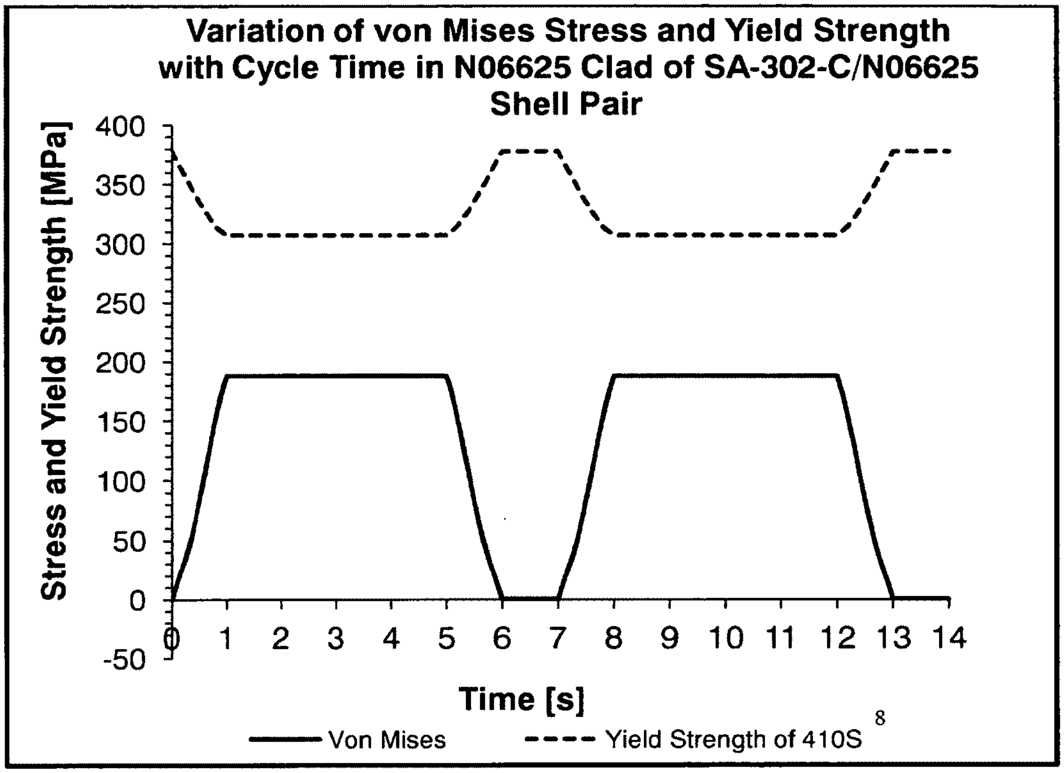

Figure 4-4: Variation of Von Mises Stress and Yield Strength with Cycle Time in the Clad of SA-302-C/N06625 Shell Pair

Figure 4-5 shows that the ratio of the maximum von Mises stress to yield strength in clad N06625 of SA-302-C/N06625 base/clad pair still remains in elastic range. The maximum value of the ratio of von Mises stress to yield strength is 61.2%.

[8] Temperature Dependant Yield Strength data is per ASME Sec II [14]

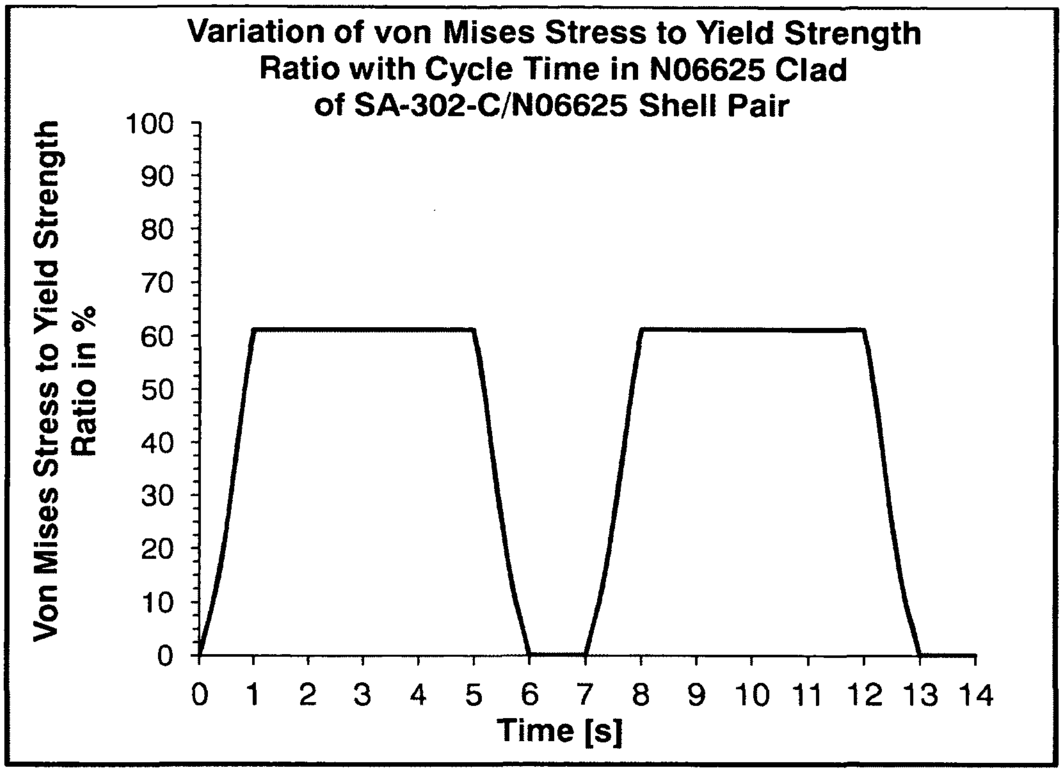

Figure 4-5: Variation of Von Mises Stress to Yield Strength Ratio with Cycle Time in the Clad of SA-302-C/N06625 Shell Pair

4. 4. 2 Axial and Hoop Stress Range for a Two-Cycle Loading Case

In previous section it was seen that 410S clad yields and plastically deforms. As a result of the plastic deformation the residual stress is present when the shell is in unloaded state. Since individual stress component range is more relevant for fatigue life than von Mises stress this section will show the difference in the axial and hoop stress ranges for the material combinations, industry adopted base SA-387-22 and clad 410S, and for new candidate material pair, base SA-302-C and clad N06625.

Figure 4-6 shows the variation of the hoop and axial stress components with cycle time in 410S clad of the SA-387-22 and 410S pair. As a result of yielding and plastic deformation during the heating-up stage of the first cycle it can be seen from Figure 4-6 that the clad 410S experiences compressive stress when the shell is unloaded. Consequently, the axial stress oscillates per cycle from 131 MPa to -167 MPa, while hoop stress oscillates from 147 MPa to -211 MPa per loading cycle. Thus, the stress range for the axial and hoop stress is 298 MPa and 358 MPa respectively.

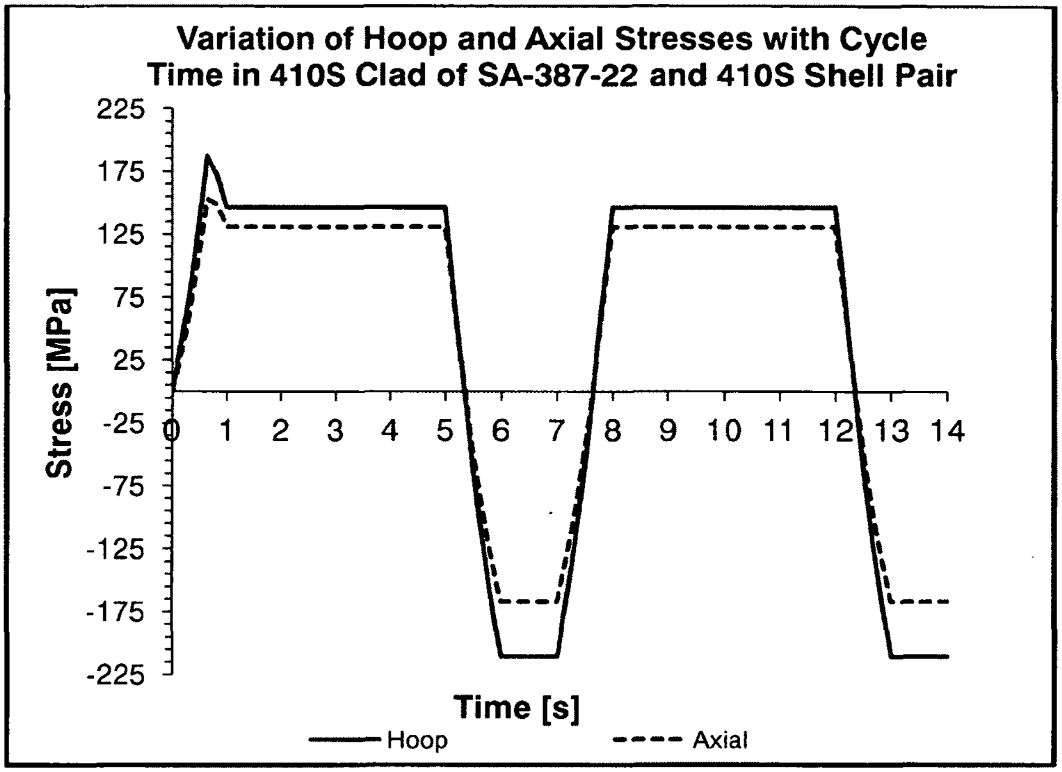

Figure 4-6: Variation of Hoop and Axial Stress with Cycle Time in the Clad of SA-387-22/410S Shell Pair

Considering the axial and hoop stress in the clad N06625 of SA-302-C and N06625 pair it can be seen from Figure 4-7 that both stress components are equal to 0 when the shell is unloaded since the clad didn't experience any plastic deformation. The maximum axial and hoop stresses in clad N06625 per cycle are 146 MPa and 212 MPa respectively. When comparing the stress ranges, the axial stress range in N06625 cladding is 49% of the axial stress range in 410S stainless steel while the hoop stress range in N06625 cladding is 59% of the hoop stress range in 410S. Hence, there is a significant reduction in the axial and hoop stress ranges in N06625 clad.

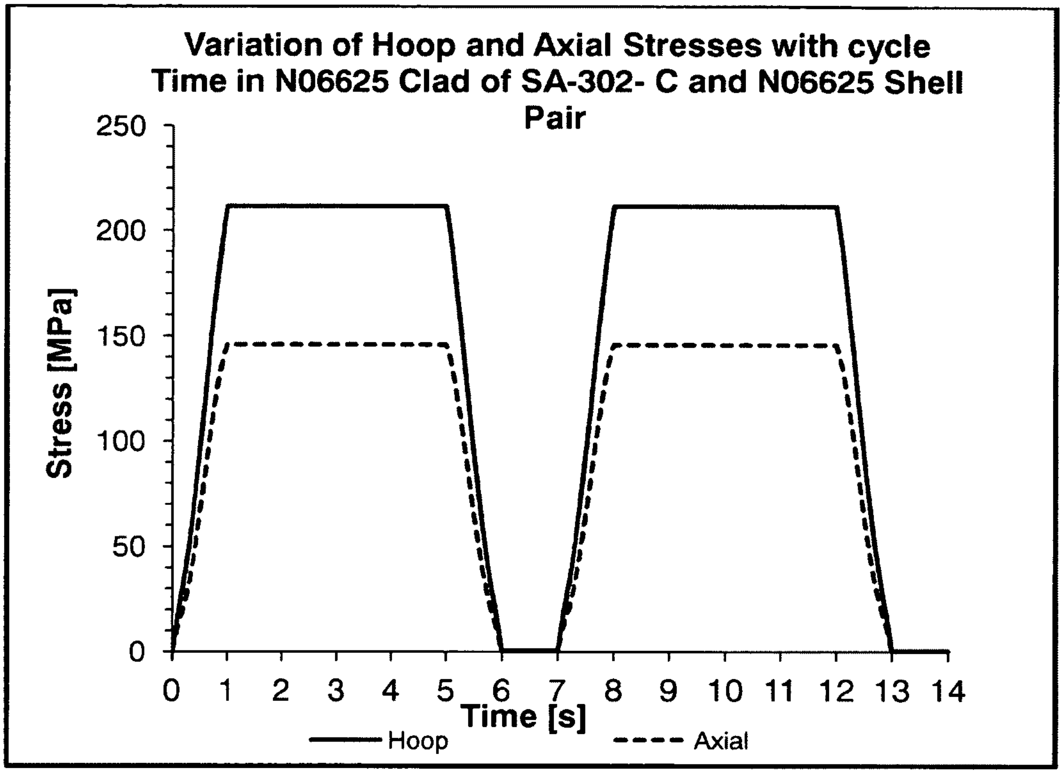

Figure 4-7: Variation of Hoop and Axial Stress with Cycle Time in the Clad of SA-302-C/N06625 Shell Pair

4. 5 Summary

Hence, the achievements are significant when using the clad and base pairs with better matching of their CTE's. The combinations of either N06600 or N06625 clad materials with any of the base materials studied revealed this achievement. Both the clad and base remained in the elastic range in comparison to the clad 410S stainless steel paired with base SA-387-22 where 410S yielded and plastically deformed. As a consequence of the yielding and plastic deformation a high compressive residual stress is present in clad 410S which significantly increased the stress range of the axial and hoop components in the clad. As it was seen above, the stress range is significantly reduced in new clad candidate N06625 when paired with SA-302-C. The much reduced stress range under the cyclic temperature and internal pressure loading could result in a much longer fatigue life of the coke drum shell.

CHAPTER 5 AXISYMMETRIC THERMO-ELASTIC FINITE ELEMENT ANALYSIS [1, 2]

5. 1 Introduction

This chapter assesses the stress level in coke drum shell for different combinations of base and clad pairs during the quenching stage. A simplified one-course model is used with only thermal loads applied to the model. This model simulates bending of coke drum shell, commonly called "vasing", caused by non-uniform temperature distribution caused by quenching water rising from the bottom of the coke drum. As for elastic-plastic analysis, ANSYS FEA software was also used for this analysis. Influence of the base CTE's, the thermal diffusivity and Young's modulus on the stress levels in the clad and base materials could be verified using this model as it was indicated in chapter 3. Ten material pairs were compared (base steels SA-387 Grades 11, 12 and 22, SA-204-C and SA-302-C paired with N06600 and N06625 high nickel alloy claddings) based on the ratio of maximum von Mises stress to yield strength. This analysis is concluded by a comparison of the axial and hoop stress ranges of a new candidate pair SA-302-C/N06625, and the industry adopted pair SA-387-22/N06625. It is shown that SA-302-C has lower stress range than SA-387-22.

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[1] A version of a part of this chapter has been published. Nikic, M., Xia, Z., 2012, "Alternative Selections of Delayed Coke Drum Materials Based on ASME Material Property Data", *Proceedings of the ASME 2012 Pressure Vessels & Piping Division Conference PVP2012*, ASME PVP2012-78548

[2] A version of a part of this chapter has been submitted for review. Nikic, M., Xia, Z., Du Plessis, P., 2012, "Assessment of Coke Drum Materials Based on ASME Material Property Data", ASME J. Pressure Vessel Technology, PVT-12-1052 (ASME PVT Journal Paper Manuscript under Review)

5. 2 Model Set-up [3, 4]

To simulate the quenching stage in coke drums an axisymmetric one-course model shown in Figure 5-1 is used. The thermo-elastic analysis model (coupled heat transfer and elastic stress analysis) in ANSYS is used. ANSYS plane 13 element with axisymmetric option is adopted. The model performs transient analysis and it takes into account temperature gradients and stresses associated with the gradients. The temperature dependant material properties are used per ASME Section II [14]. The properties are obtained at six temperatures 20, 100, 200, 300, 400 and 500 °C and entered as input into ANSYS code.

The dimensions and the constraints of the model are as follows (Shown in Figure 5.1):

a) All the dimensions of the course are maintained the same as in the elastic-plastic model except that the length of the course is extended to 2500 mm.(See explanation in section 5.2.2)

b) The loads and constraints are following:

- The bottom surface is fixed in vertical (Y) direction and free to move in radial (X) direction, in addition the surface is adiabatic.
- The top surface is free to move under "plane remains plane" condition (all nodes are coupled in (Y) direction) and it is also adiabatic surface.
- The external surface of the shell is adiabatic and free to move.

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[3] A version of this section has been published. Nikic, M., Xia, Z., 2012, "Alternative Selections of Delayed Coke Drum Materials Based on ASME Material Property Data", *Proceedings of the ASME 2012 Pressure Vessels & Piping Division Conference PVP2012*, ASME PVP2012-78548

[4] A version of this section has been submitted for review. Nikic, M., Xia, Z., Du Plessis, P., 2012, "Assessment of Coke Drum Materials Based on ASME Material Property Data", ASME J. Pressure Vessel Technology, PVT-12-1052 (ASME PVT Journal Paper Manuscript under Review)

- The entire internal surface is initially under the heat convective load of the mixture of the hot oil and coke.

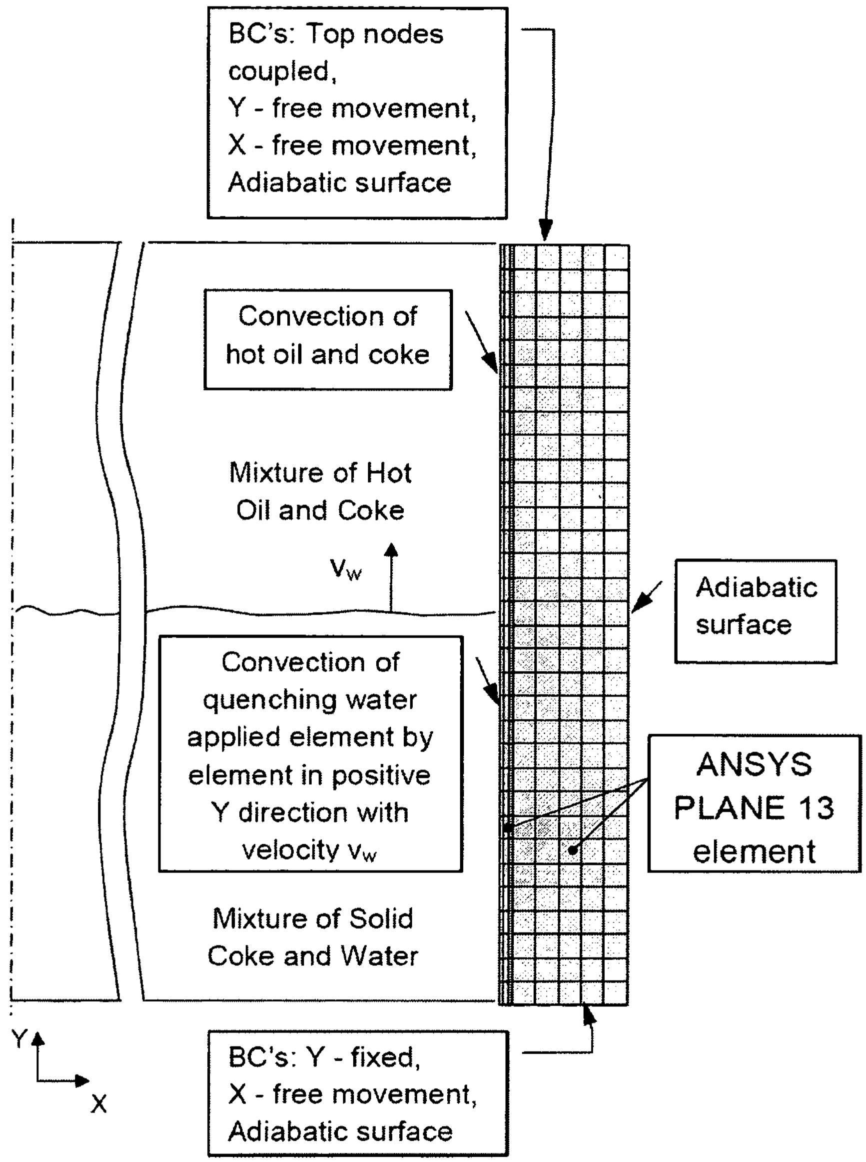

Figure 5-1: Axisymmetric Thermo-Elastic Finite Element Model (Adapted from Refs. [16, 17])

- The convective load of rising water is applied from the bottom surface element by element and advances in positive Y-direction with the velocity v_w=1 mm/s. When the convective load of the rising water is applied to the element it overrides the heat convective load of the mixture of the hot oil and coke. Since the convection of the rising water is applied element by element it is important to have sufficiently small element height such that the simulation represents the uniform rising water as close as possible.

- The initial condition temperature of the shell is 482 ^{o}C; hence, the stresses due to mismatch of the CTE's between the clad and base are taken into account.
- The bulk temperatures and the corresponding heat convection coefficients used are per Xia et. al [4] with the values:
    - Bulk temperature of the mixture of hot oil and coke is 482^{o}C
    - Bulk temperature of quenching water is 93^{o}C
    - Heat convection coefficient of the mixture of hot oil and coke is 141 W/m^{2}K
    - Heat convection coefficient of quenching water is 345 W/m^{2}K

5. 2. 1 Mesh Refinement

Since the course length is significantly longer for this model than for the elastic-plastic model a coarser mesh was used in this model. A mesh refinement method was used to validate the convergence of the thermo-elastic analysis. Since this is a transient analysis the results are dependable not only on the element size but also on the time step size. ANSYS Help Guide for transient thermal analysis [26] recommends refining elements for a chosen time step size instead of decreasing time step size for a chosen element size. The former method produces better results [26]. The maximum values of von Mises stress are measured at the middle of the course at the nodes on the internal and the external surfaces of the shell as shown in Figure 5-2.

It should be noted that von Mises stress values measured at the locations shown in Figure 5-2 are the first maximum values i.e. the values slightly above the water level where the shell is still hot (more explanation of stress locations will be provided in the following section).

Table 5-1 shows the results of the mesh refinement for the minimum time sub-step and initial sub-step of 0.25 s.

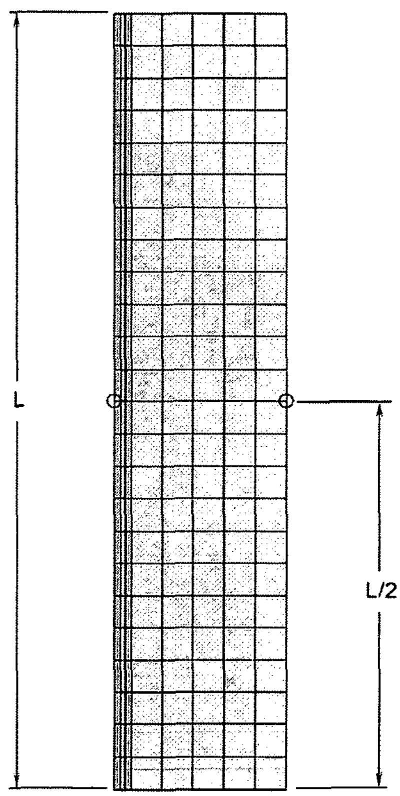

Figure 5-2: Von Mises Stress Measurement Location Nodes

As it can be seen from Table 5-1, there is no significant variation of the results with the change of the mesh indicating that the size of the elements is sufficient to produce valid results for the minimum and initial time sub-step sizes. The size of the elements in the middle row in Table 5.1 is selected for the analysis.

Table 5-1: Mesh Refinement Results

MODEL MATERIALS: BASE SA-302-C, CLAD N06625			
MINIMUM AND INITIAL SUBSTEP TIME IS 0.25 [s] WITH AUTOMATIC STEPING CONTROL ABOVE THE MINIMUM TIME			
ELEMENT SIZE [mm] WIDTH X HEIGHT		MAXIMUM VON MISES [MPa] IN THE HOT SHELL MEASURED AT 1/2 OF THE COURSE LENGTH	
CLAD	BASE	INTERNAL SURFACE	EXTERNAL SURFACE
1.27 X 10	7.62 X 10	97.695	193.504
0.847 X 5	4.572 X 5	97.683	195.201
0.635 X 2.5	2.8575 X 2.5	97.551	195.747

5. 2. 2 Validating the Required Length of the Course

It should be noted from Figure 5-3 that as the cold water is rising from the bottom of the coke drum the shell is bending. This form of bending is commonly called "vasing". Additionally it is important to note that "vasing" moves with the rising water. As indicated by Nikic et al. [16, 17] the maximum stress can be located either at the bent portion of the shell approximately just above the water level where the metal is hot or at the bent portion some distance bellow the water level where the shell temperature is lowered by the quenching water. This is illustrated in Figure 5-3. At these two locations that will be denoted as "Hot End" and "Cold End" [16, 17] the maximum stress can occur either at the internal surface of the shell (clad) or at the external surface of the shell (base).

Using one-course model the results can be affected by the top and the bottom constraints if the length of the model is not sufficient [16, 17]. The length of the model depends on the bending length designated with L_B in Figure 5-3. The bending length is measured from the maximum stress at the "Hot End" to the location bellow the bent portion at the "Cold End" where the shell starts to flatten out. This length is approximately 900 mm. It is important to note that the constraints influence the results in the range of constraint length designated with L_C in Figure 5-3. The constraint influence length has to be about the same or greater than the bending length, the results measured in the range between are valid. In this case L_C is 1000 mm.

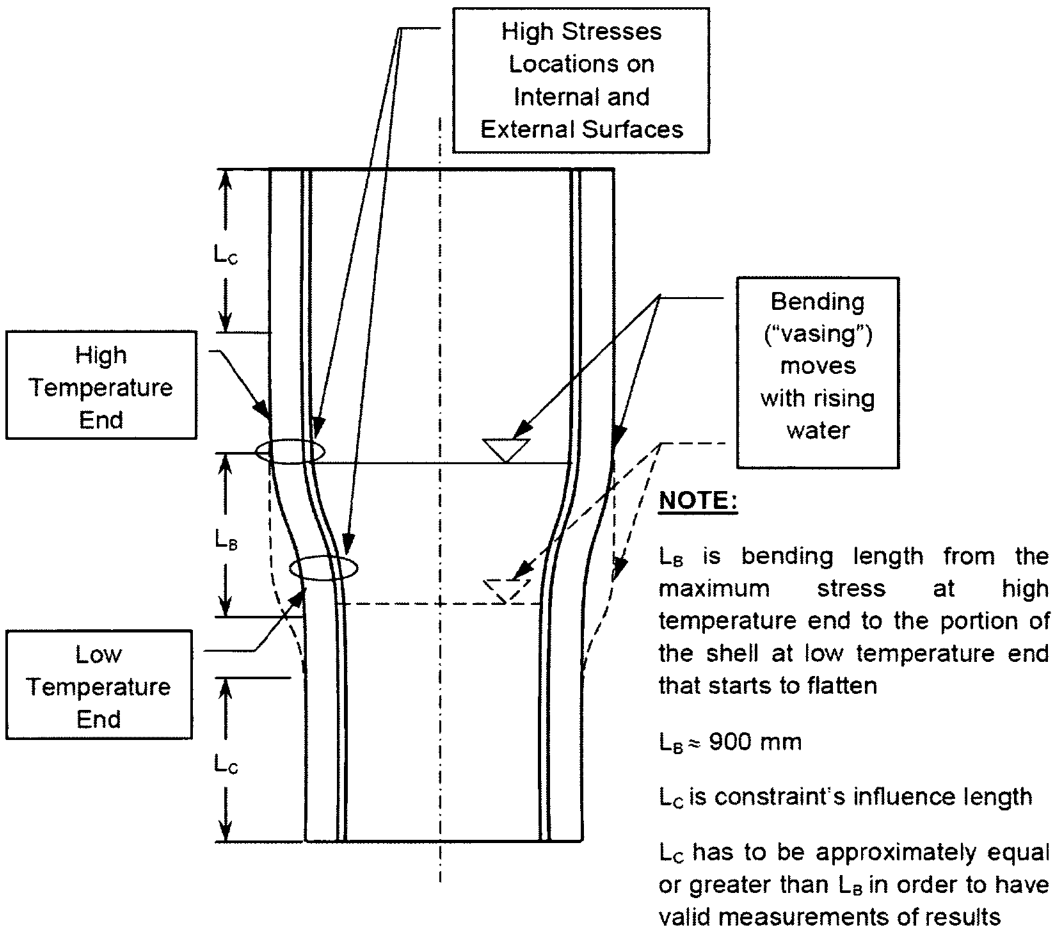

Figure 5-3: Bending of the Coke Drum Shell during Quenching Stage

The length of the model is validated by using two models of different lengths, one 2500 mm long and the second 5000 mm long. The maximum von Mises stresses are measured as per Figure 5-2, at the "Hot End" at the middle of the models at the internal and the external surfaces. The von Mises stress values are compared. From the results in Table 5-2 it can be seen that the values of von

Mises stress are not altered by using two different course lengths of 2500 mm and 5000 mm. 2500 mm long course is to be used in this study due to shorter required processing time.

Table 5-2: Validation of Required Course Length

MODEL MATERIALS: BASE SA-302-C, CLAD N06625		
COURSE LENGTH [mm]	MAXIMUM VON MISES [MPa] IN THE HOT SHELL MEASURED AT 1/2 OF THE COURSE LENGTH	
	INTERNAL SURFACE	EXTERNAL SURFACE
2500	97.683	195.201
5000	97.737	195.229

It should be noted that when the maximum stresses are measured at the "Hot End" at the location of 1000 mm away from the bottom of the course von Mises stresses at the internal and external surfaces are 97.872 MPa and 195.744 MPa respectively; thus, this validates that the measurements in the range 1000 mm away from the top and the bottom are valid.

5. 3 Quenching Stage Results

5. 3. 1 Von Mises to Yield Strength Ratio [5, 6]

During the quenching stage von Mises stresses are obtained at the hot and cold end at the clad and base as explained in the previous section. At those locations, at the same time the temperatures are also recorded.

[5] A version of this section has been published. Nikic, M., Xia, Z., 2012, "Alternative Selections of Delayed Coke Drum Materials Based on ASME Material Property Data", *Proceedings of the ASME 2012 Pressure Vessels & Piping Division Conference PVP2012*, ASME PVP2012-78548

[6] A version of this section has been submitted for review. Nikic, M., Xia, Z., Du Plessis, P., 2012, "Assessment of Coke Drum Materials Based on ASME Material Property Data", ASME J. Pressure Vessel Technology, PVT-12-1052 (ASME PVT Journal Paper Manuscript under Review)

The yield strength of the materials is obtained from ASME Section II [14] at these temperatures. The ratio of von Mises stress to yield strength is then calculated and expressed in percent. At the moment when this ratio reaches 100% material reaches its yield point. From the results shown in Table 5-3 the following can be noted:

- At "Cold End" all materials remain in the elastic range.
- At "Hot End" , for the base steels, either paired with N06625 or N06600 clad the following is observed:
  - SA-387 grades 11, 12 and 22 (Chrome Molybdenum steels) all yield.
  - SA-204-C remains in the elastic range slightly below the yield strength of the base.
  - SA-302-C remains in the elastic range with the von Mises to Yield strength ratio of 81.1% and 80.3 % when paired with N06600 and N06625 respectively.
- As seen, the base SA-302-C has the lowest von Mises to yield strength compared to the other base steels. The comparison of the von Mises to yield strength ratio of cladding materials N06625 and N06600 paired with this base steel reveals that N06625 remains far in the elastic range at the "Hot End" with the ratio of 31.9% while N06600 is close to yielding. This is because clad N06625 has slightly lower CTE than the CTE of the base SA-302-C which results in some tensile stress in the clad when the shell is hot. Part of the compressive stress in the clad caused by bending of the shell

at the "Hot End" is being cancelled out by the tensile stress in the clad produced by the mismatch in the CTE's between N06625 clad and SA-302-C base of the shell at the "Hot End" and reduces overall stress in the clad at this end. It should be noted that when CTE of the clad is lower than CTE of the base, as in this case, results in a positive outcome; however, it should be emphasized that the difference in the CTE's should be small such that it does not cause the yielding of the clad when the shell is hot.

Table 5-3: Results of Thermo-Elastic Analysis during Quenching Stage [16, 17] (Reprinted with Permission from ASME)

BASE/CLAD PAIR	SA-387-12 Cl. 2/N06600 SB-168 H.R.				SA-387-12 Cl. 2/N06625 SB-443 Gr. 1 ANN.			
MEASUREMENT LOCATION	HOT END		COLD END		HOT END		COLD END	
	BASE	CLAD	BASE	CLAD	BASE	CLAD	BASE	CLAD
TEMPERATURE [°C]	477	481	213	199	477	482	214	222
VON MISES STRESS [MPa] AT TEMPERATURE	221	227	143	133	218	132	143	156
YIELD STRENGTH [MPa] AT TEMPERATURE	189	203	223	220	189	307	223	341
VON MISES/ YIELD RATIO IN %		111.8	64.1	60.5		43.0	64.1	45.7
BASE/CLAD PAIR	SA-387-11 Cl. 2/N06600 SB-168 H.R.				SA-387-11 Cl. 2/N06625 SB-443 Gr. 1 ANN.			
MEASUREMENT LOCATION	HOT END		COLD END		HOT END		COLD END	
	BASE	CLAD	BASE	CLAD	BASE	CLAD	BASE	CLAD
TEMPERATURE [°C]	477	481	213	199	477	482	214	221
VON MISES STRESS [MPa] AT TEMPERATURE	221	227	143	133	218	132	143	156
YIELD STRENGTH [MPa] AT TEMPERATURE	212	203	260	220	212	307	260	341
VON MISES/ YIELD RATIO IN %		111.8	55.0	60.5		43.0	55.0	45.7
BASE/CLAD PAIR	SA-387-22 Cl. 2/N06600 SB-168 H.R.				SA-387-22 Cl. 2/N06625 SB-443 Gr. 1 ANN.			
MEASUREMENT LOCATION	HOT END		COLD END		HOT END		COLD END	
	BASE	CLAD	BASE	CLAD	BASE	CLAD	BASE	CLAD
TEMPERATURE [°C]	478	482	212	198	477	482	214	220
VON MISES STRESS [MPa] AT TEMPERATURE	233	228	150	136	230	132	149	159
YIELD STRENGTH [MPa] AT TEMPERATURE	224	203	262	220	224	307	261	341
VON MISES/ YIELD RATIO IN %		112.3	57.3	61.8		43.0	57.1	46.6
BASE/CLAD PAIR	SA-204-C/N06600 SB-168 H.R.				SA-204-C/N06625 SB-443 Gr. 1 ANN.			
MEASUREMENT LOCATION	HOT END		COLD END		HOT END		COLD END	
	BASE	CLAD	BASE	CLAD	BASE	CLAD	BASE	CLAD
TEMPERATURE [°C]	477	481	213	199	477	482	214	222
VON MISES STRESS [MPa] AT TEMPERATURE	200	227	140	132	197	133	139	155
YIELD STRENGTH [MPa] AT TEMPERATURE	208	203	257	220	208	307	257	341
VON MISES/ YIELD RATIO IN %	96.2	111.8	54.5	60.0	94.7	43.3	54.1	45.5
BASE/CLAD PAIR	SA-302-C/N06600 SB-168 H.R.				SA-302-C/N06625 SB-443 Gr. 1 ANN.			
MEASUREMENT LOCATION	HOT END		COLD END		HOT END		COLD END	
	BASE	CLAD	BASE	CLAD	BASE	CLAD	BASE	CLAD
TEMPERATURE [°C]	477	481	209	207	477	481	211	229
VON MISES STRESS [MPa] AT TEMPERATURE	198	189	141	168	196	98	140	193
YIELD STRENGTH [MPa] AT TEMPERATURE	244	203	304	220	244	307	304	339
VON MISES/ YIELD RATIO IN %	81.1	93.1	46.4	76.4	80.3	31.9	46.1	56.9

Figure 5-4 shows the difference of von Mises stress between SA-387-22 and SA-302-C graphically during the coke drum quenching stage. The first peak corresponds to the maximum values at "Hot End" while the second peak in the graph corresponds to the values at "Cold End". It should be noted that along the quenching cycle the difference in von Mises stress between SA-387-22 and SA-302-C increases as the stress increases.

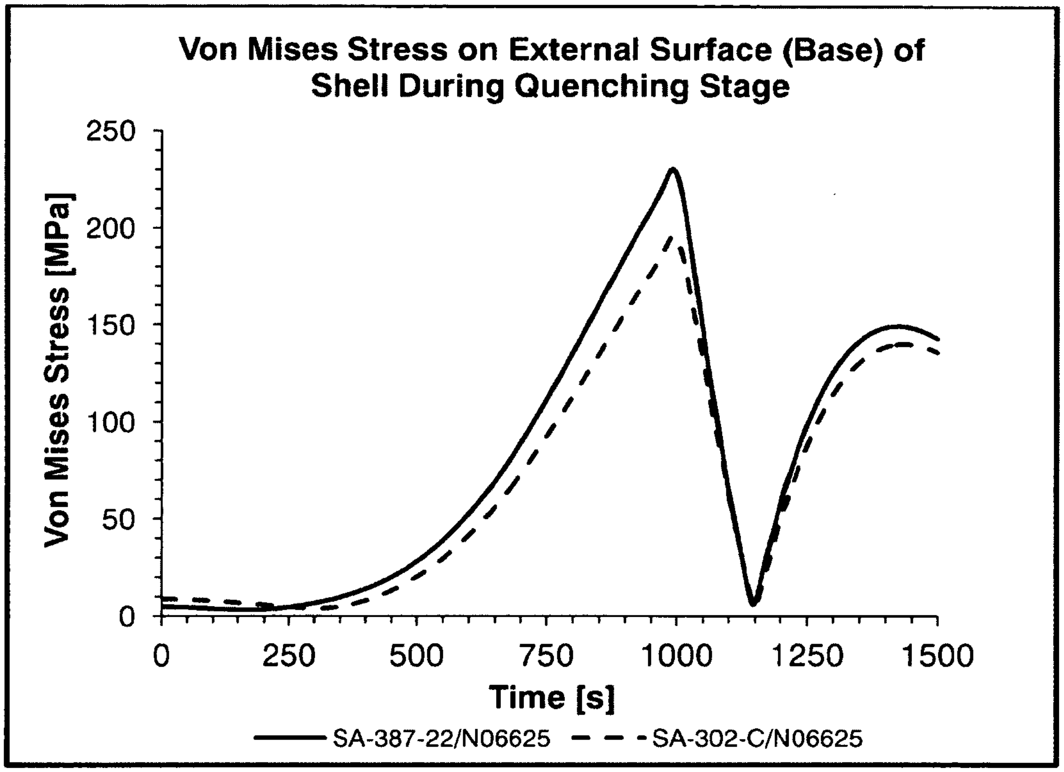

Figure 5-4: Comparison of Von Mises Stresses at the External Surface for Base Steels SA-387-22 and SA-302-C during Quenching Stage

5. 3. 2 Axial and Hoop Stress Range

The difference in the stress range for the axial and the hoop stress is examined between the new candidate base SA-302-C paired with N06625 and industry adopted base SA-387-22 also paired with N06625. The axial stress range for these materials is shown in Figure 5-5. It can be seen that the new base candidate material has smaller stress range.

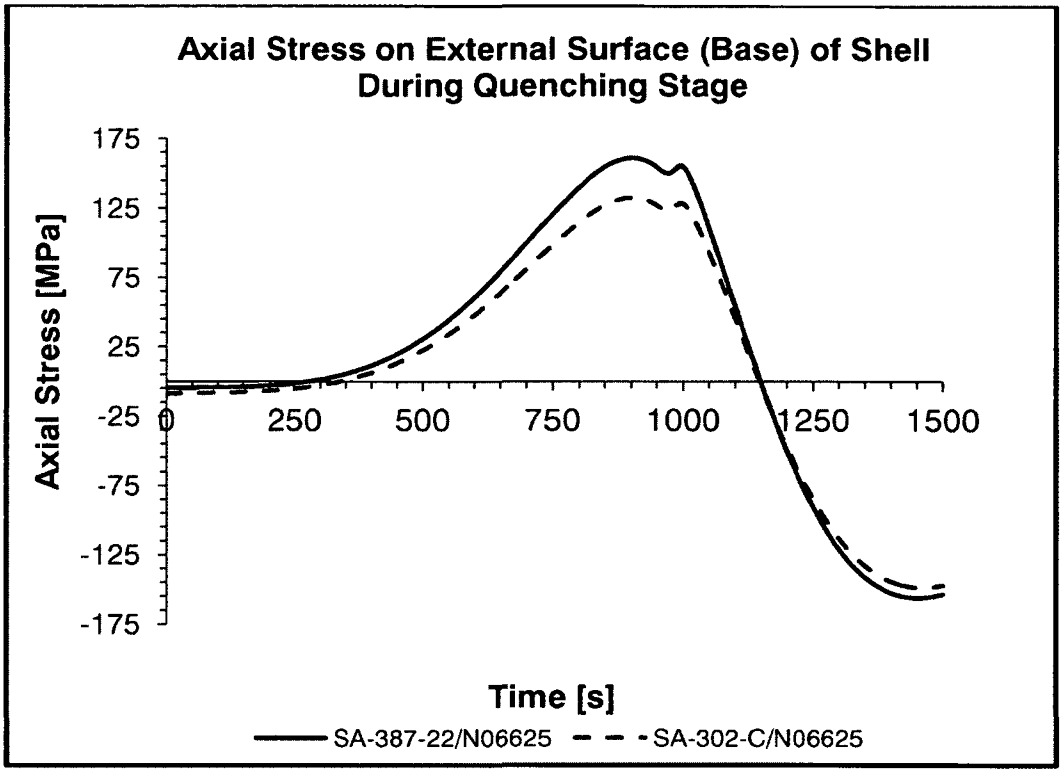

Figure 5-5: Comparison of Axial Stresses at the External Surface for Base Steels SA-387-22 and SA-302-C during Quenching Stage

Table 5-4 compares the axial stress ranges at the external surfaces of the base steels. The axial stress ranges for SA-387-22/N06625 and SA-302-C/N06625 pairs are 317 MPa and 281MPa, respectively. Thus, the axial stress range of the new base candidate SA-302-C is 11.4% lower than the stress range of SA-387-22.

Table 5-4: Comparison of Axial Stress Ranges at the External Surface for Base Steels SA-387-22 and SA-302-C during Quenching Stage

MATERIAL BASE/CLAD	MAXIMUM AXIAL STRESS [MPa]	MINIMUM AXIAL STRESS [MPa]	AXIAL STRESS RANGE[MPa]
SA-387-22/N06625	161	-156	317
SA-302-C/N06625	132	-149	281
AXIAL STRESS RANGE DIFFERENCE:			36

Considering the hoop stresses, the same trend is followed as in the case of the axial stress range as shown in Figure 5-6. Table 5-5 shows the numerical values of stress ranges. It can be seen from Table 5-5 that the hoop stress ranges for SA-387-22 and SA-302-C base steels are 142 MPa and 120 MPa respectively. Thus, it can be seen that SA-302-C results in 15.5% lower hoop stress range than SA-387-22.

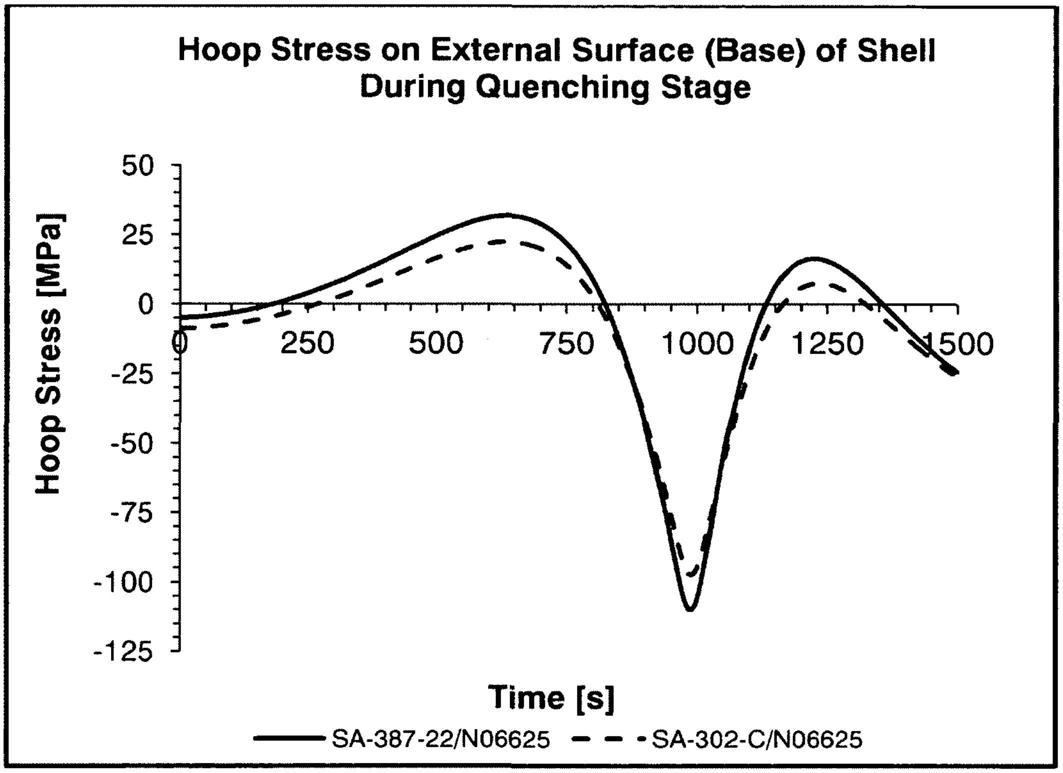

Figure 5-6: Comparison of Hoop Stresses at the External Surface for Base Steels SA-387-22 and SA-302-C during Quenching Stage

Table 5-5: Comparison of Hoop Stress Ranges at the External Surface for Base Steels SA-387-22 and SA-302-C during Quenching Stage

MATERIAL BASE/CLAD	MAXIMUM HOOP STRESS [MPa]	MINIMUM HOOP STRESS [MPa]	HOOP STRESS RANGE[MPa]
SA-387-22/N06625	32	-110	142
SA-302-C/N06625	22	-98	120
HOOP STRESS RANGE DIFFERENCE:			22

5. 3. 3 Influence of Thermal Diffusivity of Base and Clad Materials on Stress Level in Coke Drum Shell

As mentioned in section 3.2.3 the variation of the thermal diffusivities among the materials considered may influence the stress level during the quenching stage. Two FE analyses were carried for verification of this assumption. The thermal diffusivities of the following materials (shown in Figure 5-7) are chosen for the analyses:

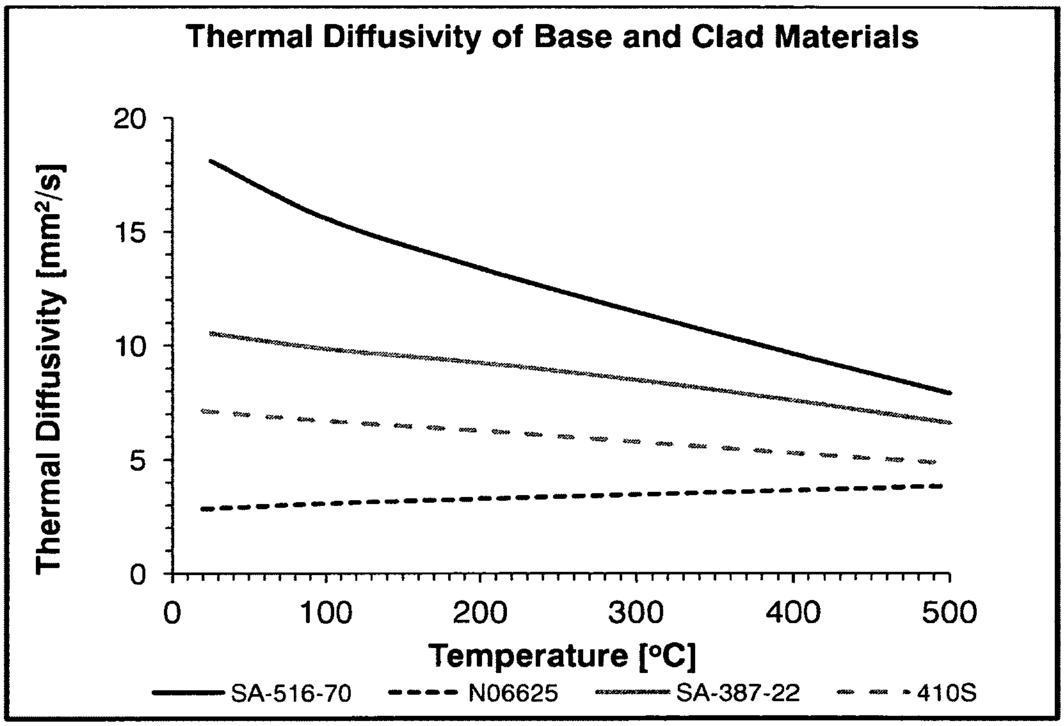

Figure 5-7: Thermal Diffusivity of Different base and Clad Materials (Data per Ref [14])

1) The base with the highest thermal diffusivity among the materials studied is Carbon Steel (SA-516-70) paired with the clad N06625 that has the lowest thermal diffusivity among the clad materials studied.

2) The base with the lowest thermal diffusivity among the materials studied is SA-387-22 paired with the clad 410S that has the highest thermal diffusivity of the clad materials studied.

To determine the influence on the stress level merely by the variation of the thermal diffusivity properties two finite element analyses were carried out, FEA-1 and FEA-2. These two analyses are only different with respect to the input properties of the thermal diffusivities in order to see their influence on the stress level [17]. This is shown in Figure 5-8. Thus, any variation in the stress will correspond to the variation of the thermal diffusivities.

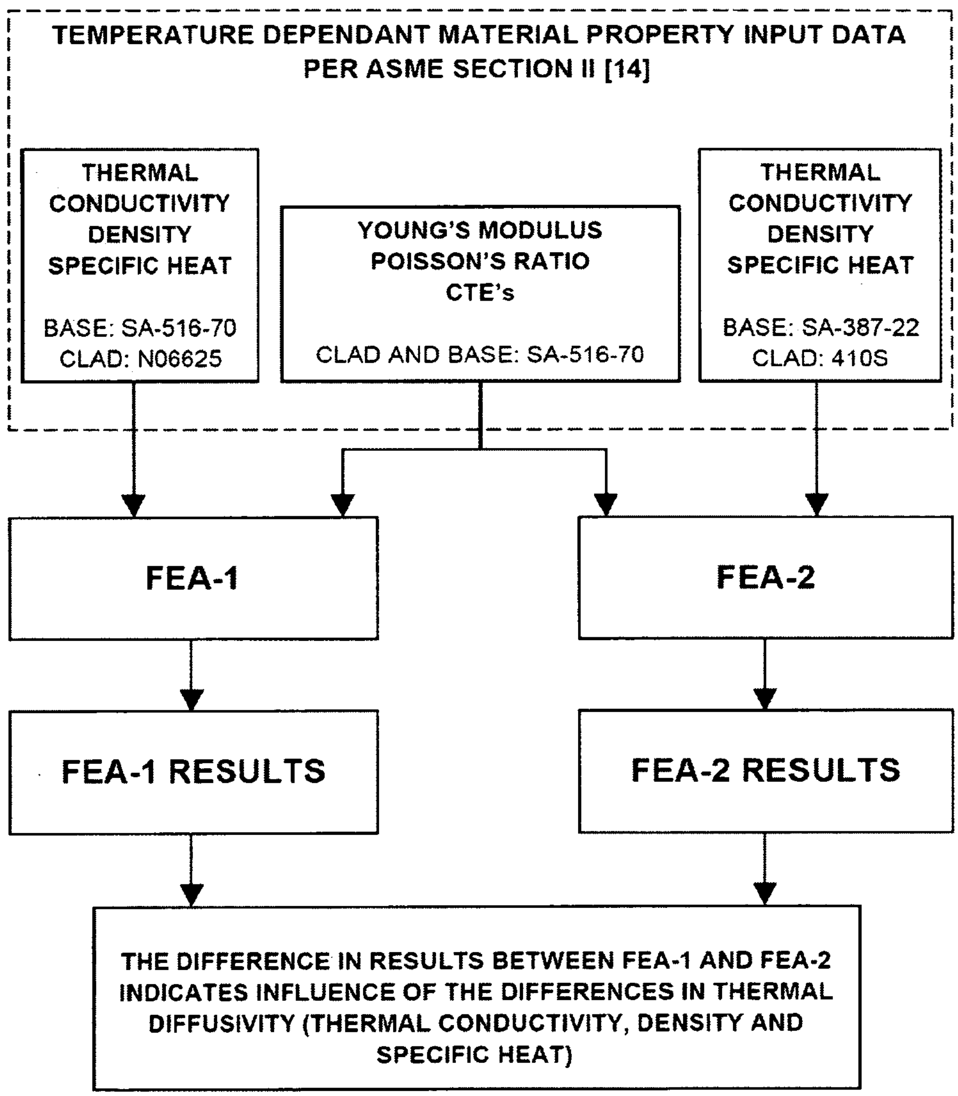

Figure 5-8: Input Data Block Diagram for Assessment of Influence of Thermal Diffusivities of Base and Clad Materials on Stress Level in Coke Drum Base [7]

[7] Figure 5-8 uses the same set of materials as per Ref [17]

It should be noted that the input in Figure 5-8 is given in terms of thermal conductivity, density and specific heat. Thermal diffusivity is expressed in terms of thermal conductivity divided by the product of density and specific heat [27]. ANSYS takes as the input the properties that define thermal diffusivity; thus ANSYS uses thermal conductivity, density and specific heat as the input to define thermal diffusivity.

Figure 5-9 shows that during coke drum quenching stage with raising water there is almost no difference in the stress level in the clad at the "Hot End" (First peak in the graph) and also a small difference at the "Cold End" (Second Peak in the graph).

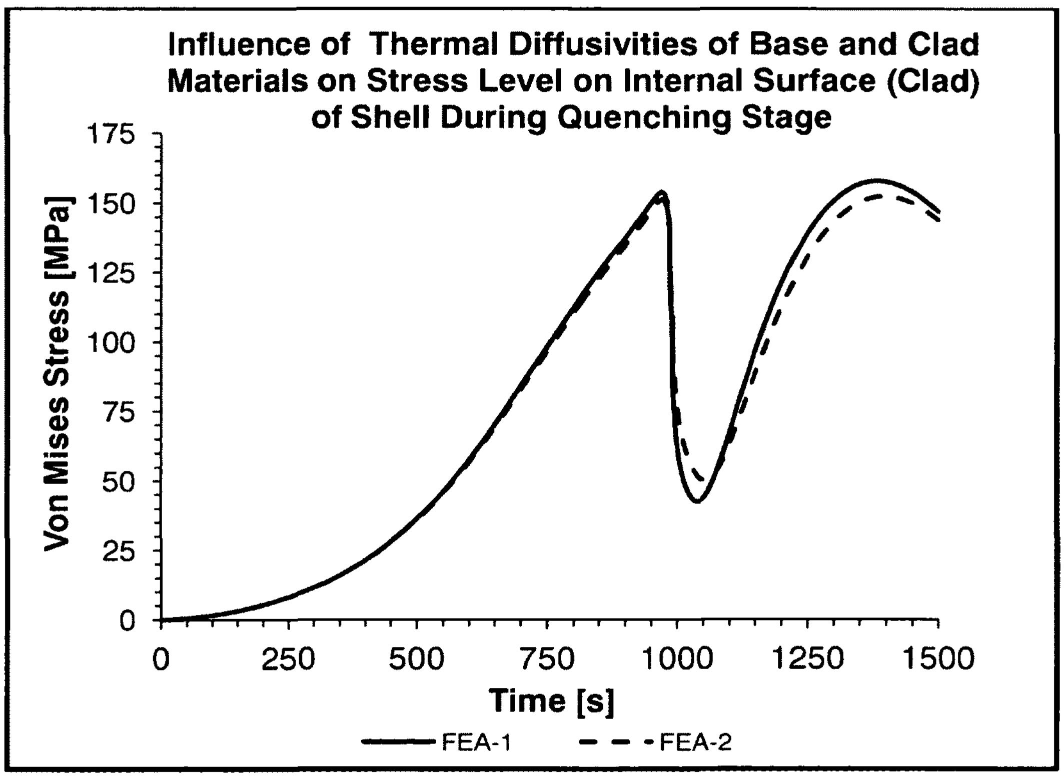

Figure 5-9: Influence of Thermal Diffusivity Properties of Base and Clad Materials on Von Mises Stress on the Internal Surface (clad) of the Coke Drum Shell During Coke Drum Quenching Stage

Figure 5-10 shows that in the base at the external surface the graph curves nearly overlap. This means that there is no difference in the stress level in the base caused by the difference in thermal diffusivities.

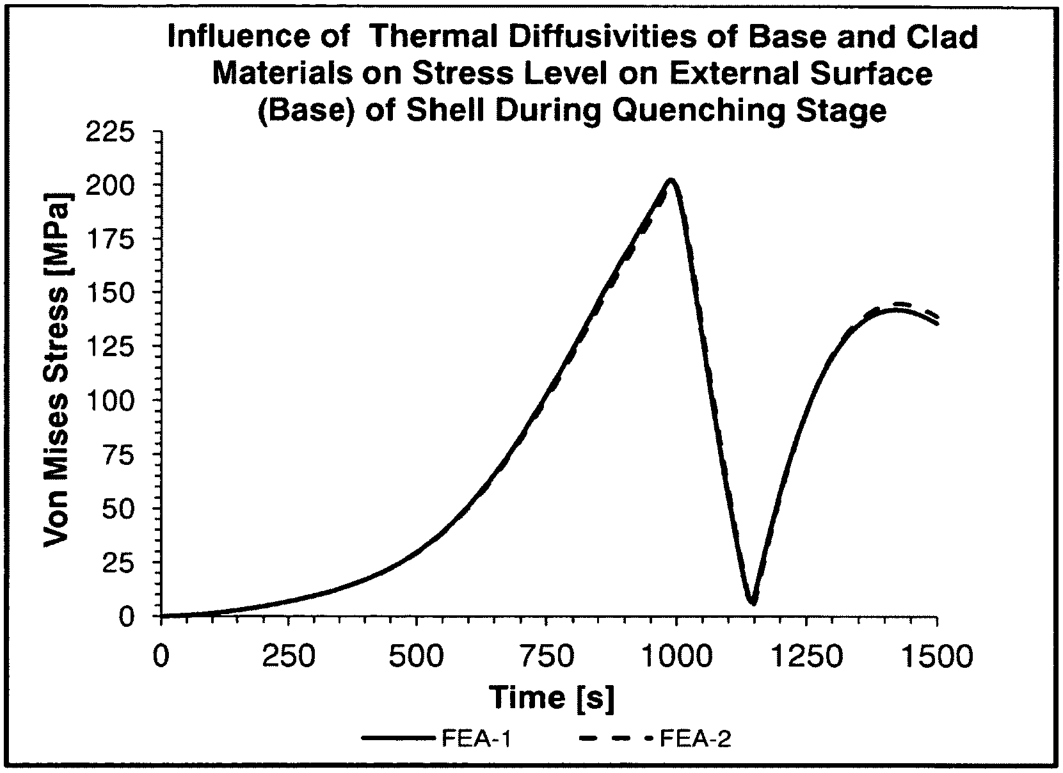

Figure 5-10: Influence of Thermal Diffusivity Properties of Base and Clad Materials on Von Mises Stress on the External Surface (base) of the Coke Drum Shell During Coke Drum Quenching Stage

5. 3. 4 Influence of Young's Modulus of Base on Stress Level in Coke Drum Shell

It was also mentioned in section 3.2.3 that Young's modulus may influence the stress level in the base of shell. Figure 5-11 shows the difference in Young's modulus between the new candidate base material SA-302-C and industry adopted base steel SA-387-22.

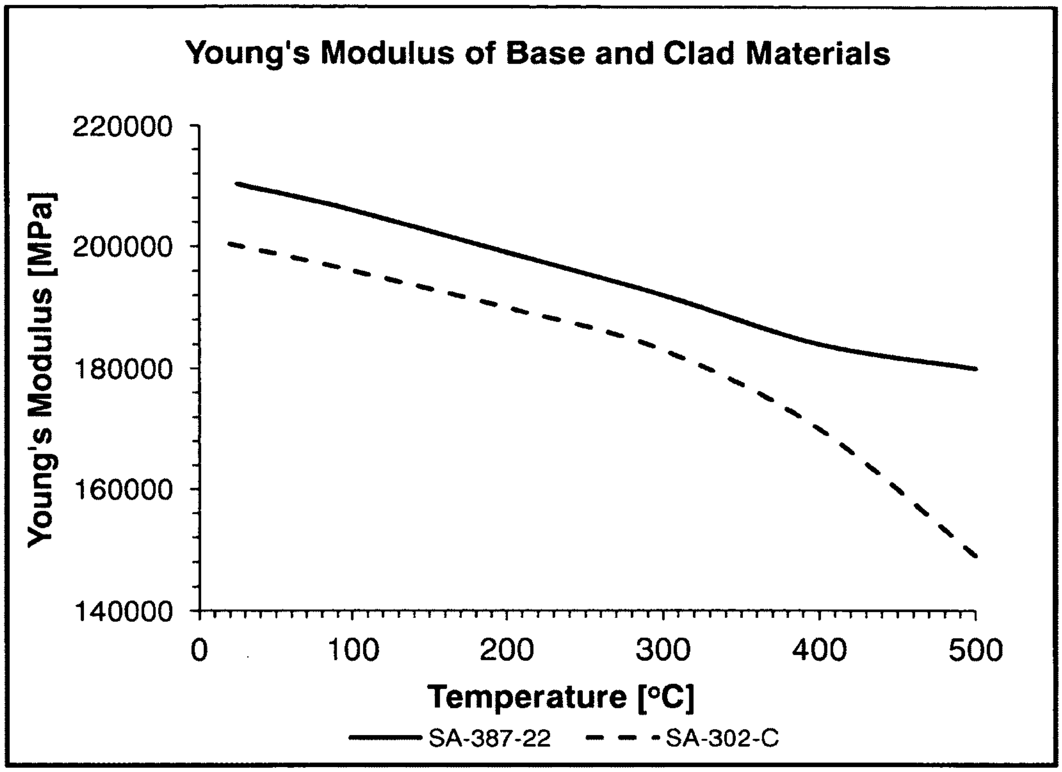

Figure 5-11: Difference in Young's Modulus between SA-387-22 and SA-302-C Base Steels (Data per Ref. (14)]

To examine how much difference in stress level is introduced by the difference in Young's modulus between the two base steels the same approach is used as in the previous section. Thus, two finite element analyses are performed, FEA-1 and FEA-2. In this case, the input material properties for the two analyses are different just with respect to the Young's modulus [17]. For clarity this approach is shown in Figure 5-12.

FEA-1 uses Young's modulus of SA-387-22, while FEA-2 uses Young's modulus of SA-302-C. Thus FEA-1 has as an input the higher values of Young's modulus than FEA-2. It should be noted that the CTE's are taken from SA-387-22 and the CTE's are the same for both, clad and base in both analyses. The other properties are as well common for both analyses as per Figure 5-12.

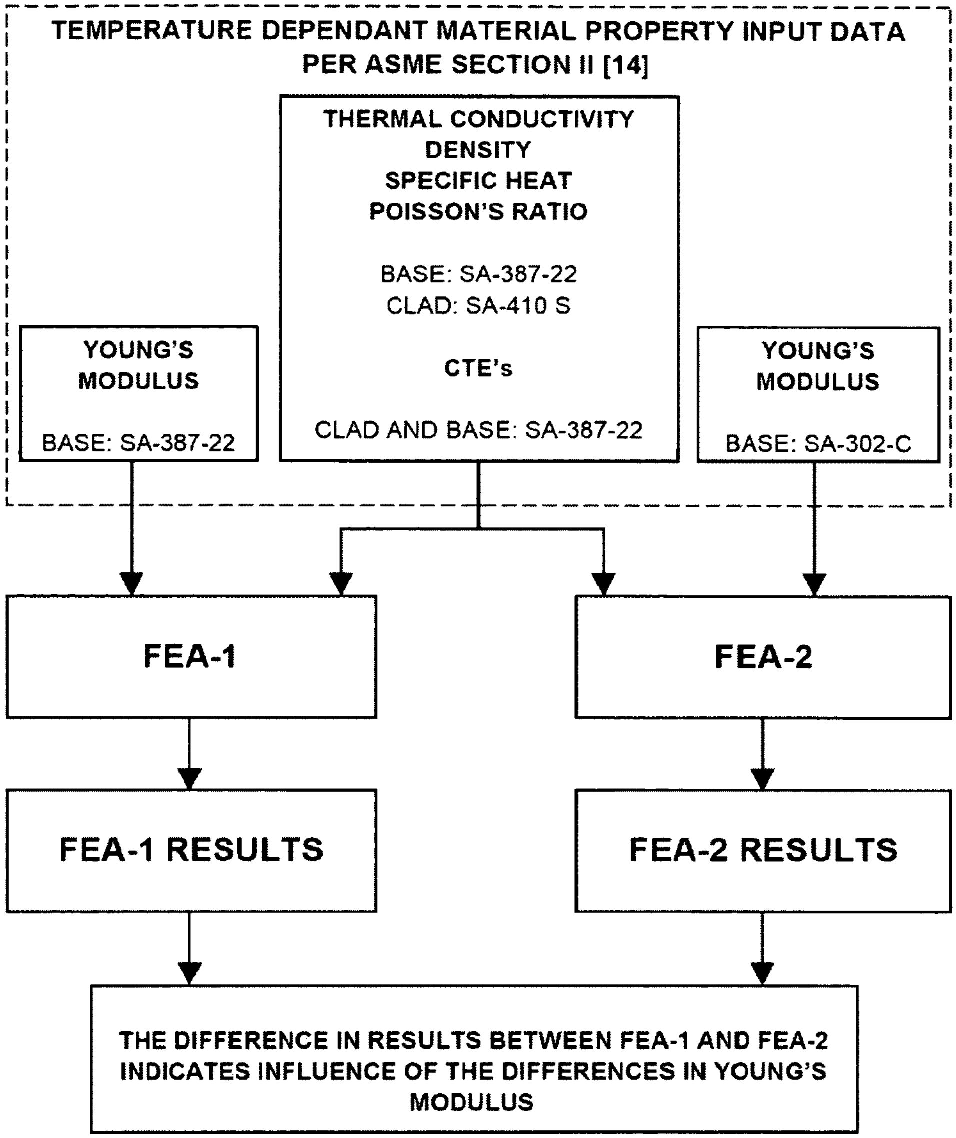

Figure 5-12: Input Data Block Diagram for Assessment of Influence of Young's Modulus of Base and Steels on Stress Level in Coke Drum Base [8]

Figure 5-13 shows the difference in von Mises stress for FEA-1 and FEA-2 during the quenching stage caused by the differences in Young's modulus.

[8] Figure 5-12 uses the same set of materials as per Ref [17]

The difference in the stress reaches 32 MPa at the high temperature end [17] (first peak in the graph). It should be recalled from Table 5-3 that the difference in von Mises stresses at the "Hot End" in the bases for SA-302-C/N06625 and SA-387-22/N06625 is 34 MPa. Hence, this difference in the stress is predominantly caused by the differences in Young's modulus [17].

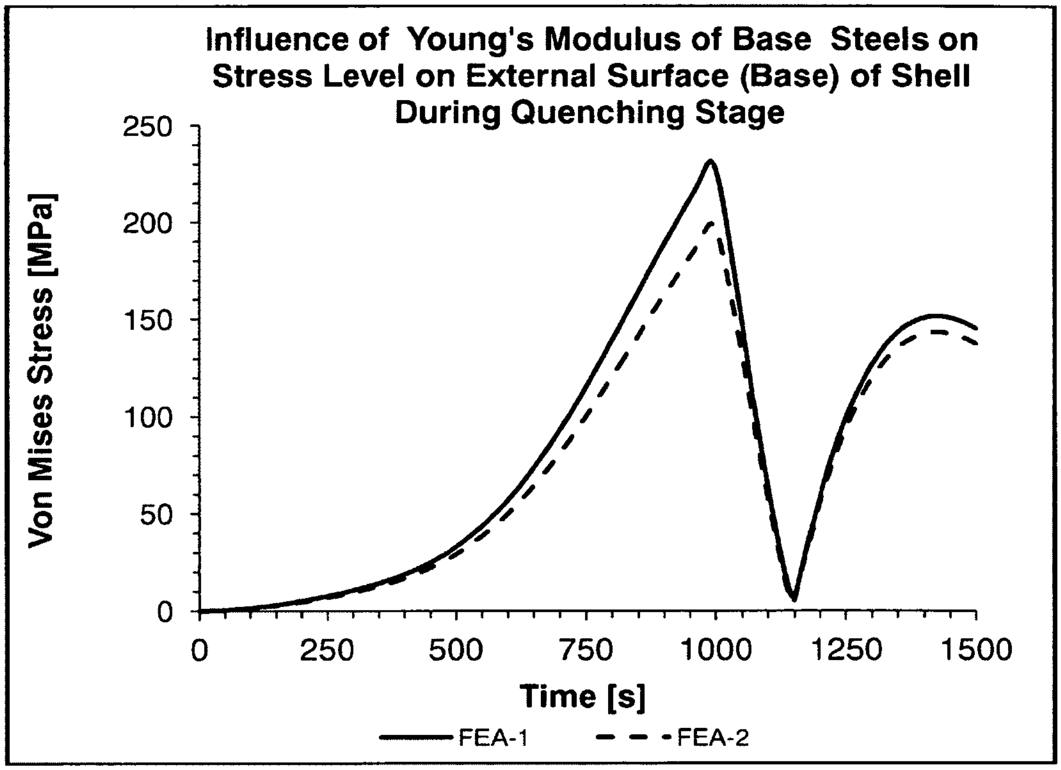

Figure 5-13: Influence of Young's Modulus of Base Steels on Von Mises Stress on the External Surface (base) of Coke Drum Shell

Additionally, from above it can be concluded that the differences in CTE's between the base steels have negligible influence on the stress level during the quenching stage.

In addition to the reduction of von Mises stress it can be seen that lower Young's modulus is beneficial since it reduces the axial stress range as shown in

Figure 5-14. Table 5-6 shows the numerical values of the axial stress range. The stress range for FEA-1 is 325 MPa and for FEA-2 it is 292.7 MPa.

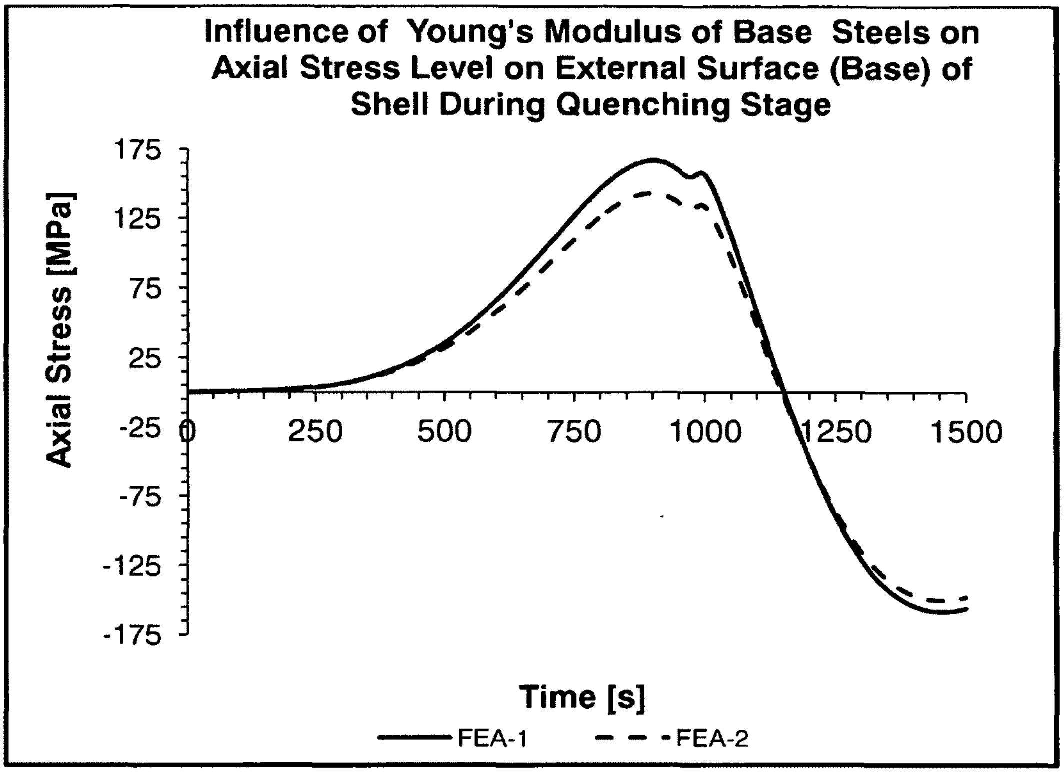

Figure 5-14: Influence of Young's Modulus of Base Steels on Axial Stress on the External Surface (base) of Coke Drum Shell

Table 5-6: Influence of Young's Modulus on Axial Stress Range on the External Surface of the Base

ANALYSIS	MAXIMUM AXIAL STRESS [MPa]	MINIMUM AXIAL STRESS [MPa]	AXIAL STRESS RANGE[MPa]
FEA-1	166.5	-158.5	325
FEA-2	142.5	-150.2	292.7

Figure 5-15 shows the influence of Young's modulus on the hoop stress range at the external surface of the base. The numerical values of the maximum and minimum hoop stresses for FEA-1 and FEA-2 are shown in Table 5-7. It can be seen from Table 5-7 that the stress range for the hoop stress is smaller than that of axial stress. The stress range for FEA-1 is 145.3 MPa and for FEA-2 the hoop stress range is 126.5.

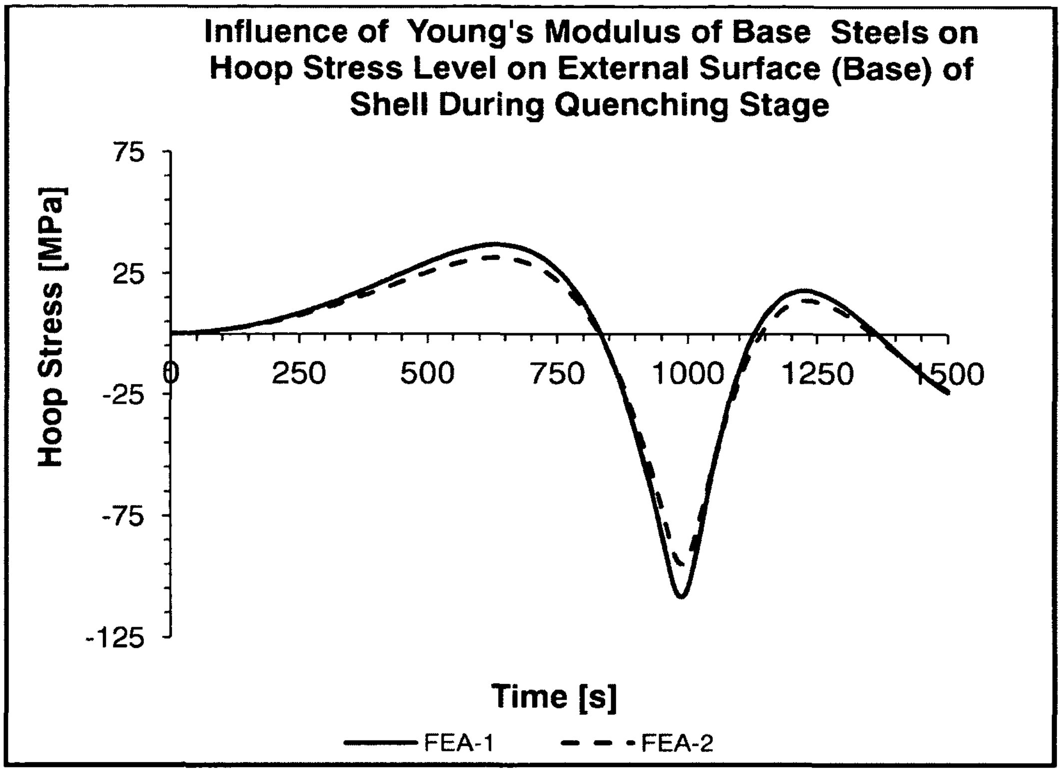

Figure 5-15: Influence of Young's Modulus of Base Steels on Hoop Stress on the External Surface (base) of Coke Drum Shell

Table 5-7: Influence of Young's Modulus on Hoop Stress Range on the External Surface of the Base

ANALYSIS	MAXIMUM HOOP STRESS [MPa]	MINIMUM HOOP STRESS [MPa]	HOOP STRESS RANGE[MPa]
FEA-1	36.8	-108.5	145.3
FEA-2	31.5	-95	126.5

5. 4 Summary

The results of this chapter have shown that SA-302-C as a base material paired with N06625 exceeds in performance the other materials pairs studied. Additionally, it was shown that during the quenching stage the Young's modulus affects the stress level. The lower values of Young's modulus decrease von

Mises stress, axial stress range and hoop stress range. As a result the new candidate base SA-302-C doesn't yield due its lower Young's modulus and higher yield strength while all other base materials studied (except SA-204-C that remains slightly below its yield point) yield. In addition SA-302-C has lower axial stress range and hoop stress range as it was shown in this chapter.

CHAPTER 6 DISCUSSION AND CONCLUSSION

6. 1 Discussion

The industry selection of materials for delayed coke applications followed the trend of increasing use of base steels with higher Chrome and Molybdenum contents and increased use of 410S stainless steel as clad material [3]. The comparison of eleven material pairs in this study has shown that SA-302-C as a base material paired with N06625 as a clad material performs significantly better. This discussion will compare the new candidate material pair SA-302-C/N06625 and currently industry adopted material and also the comparison will be made only for base materials SA-302-C and SA387-22 paired with N06625.

1) Comparison of the results between SA-302-C/N06625 and currently industry adopted SA-387-22/410S for two cycle elastic-plastic model when the maximum temperature of 482°C and the maximum pressure of 0.72 MPa are reached:

- For SA-387-22 and 410S pair the clad yields before the maximum temperature of 482°C and the maximum pressure of 0.72 MPa are reached.
- For SA-302-C and N06625 pair the maximum von Mises stress to yield strength of the clad is 61.2% when the maximum temperature of 482 °C and the pressure of 0.72 MPa are reached, thus the clad remains in the elastic range.

- For SA-387-22 and 410S pair the stress ranges in the clad are the following:
  - Axial Stress: -167 MPa to 131 MPa with the corresponding stress range of 298 MPa
  - Hoop Stress: -211 MPa to 147 MPa with the corresponding stress range of 358 MPa
- For SA-302-C and N06625 base and clad pair the stress ranges in the clad are the following:
  - Axial Stress: 0 MPa to 146 MPa with the corresponding stress range of 146 MPa
  - Hoop Stress: 0 MPa to 212 MPa with the corresponding stress range of 212 MPa

The studies by Xia et al. [4] and Ju et al. [5] have shown that a relatively thin 410S stainless steel clad compared to the thickness of base steel could yield under the thermal load due to greater mismatch of CTEs between the base and clad. The results of this study have shown that a significant achievement is made due to the closer matching of CTEs between SA-302-C base and high nickel alloy, N06625, and significantly higher yield strength of N06625 compared to that of 410S. Hence, for the combination of SA-302-C/N06625 the clad N06625 result in the maximum von Mises stress to yield strength ratio of 61.2% while for SA-387-22/410S pair at the same condition the clad yielded and plastically deformed. Since the yielding and the plastic deformation of the clad was avoided in the new candidate pair SA-302-C/N06625 the stress range of individual stress component has been significantly reduced. Hence, the axial stress range reduction in clad N06625 compared to that of clad 410S is 51% while hoop stress range reduction is 40.8 %.

2) Comparison of the results between SA302-C/N06625 and SA387-22/N06625 (and other base materials paired with N06625) for thermo-elastic model during the quenching stage further shows advantage of base SA302-C:

- For SA-387-22 and N06625 base and clad pair the maximum von Mises to yield strength ratio in the base is 102.7% [16, 17], thus the base yields.
- For SA-302-C and N06625 base and clad pair the maximum von Mises to yield strength ratio in the base is 80.3% [16, 17], thus the base remains elastic.
- For SA-387-22 and N06625 base and clad pair the stress ranges in the base are the following:
    - Axial Stress: -156 MPa to 161 MPa with the corresponding stress range of 317 MPa
    - Hoop Stress: -110 MPa to 32 MPa with the corresponding stress range of 142 MPa
- For SA-302-C and N06625 base and clad pair the stress ranges in the base are the following:
    - Axial Stress: -149 MPa to 132 MPa with the corresponding stress range of 281 MPa

- Hoop Stress: -98 MPa to 22 MPa with the corresponding stress range of 120 MPa

Additional improvement in the stress reduction, shown above, in the base during quenching stage is achieved due to lower Young's modulus of SA-302-C steel as a base material. It was shown that during quenching the differences in CTE's and the thermal diffusivities of the base steels studied do not affect much the stress level in the base. The lower Young's modulus of SA-302-C contributes to the reduction of von Mises stress in the base of 32 MPa [17] at the hot end of the shell during the quenching stage in comparison to that of SA-387-22. While SA-387- grades 11, 12 and 22 combined with N06625 all yield and SA-204-C combined with N06625 remains slightly below yield point, under the same loading condition SA-302-C paired with N06625 results in a ratio of 80.3% of the maximum von Mises stress to yield strength. Comparing the yield strengths at the temperature (477 ^{o}C) at which the von Mises stresses are measured to be 224 MPa and 244 MPa for SA-387-22 and SA-302-C respectively [16, 17] and 32 MPa reduction in the von Mises stress due to lower Young's modulus [17] it can be concluded that the contribution of lower Young's modulus to the reduction of von Mises to yield ratio is greater than the contribution caused by the increase in the yield strength from SA-387-22 to SA-302-C. In addition, the lower Young's modulus of SA-302-C decreased the axial and hoop stress range in this material during the quenching stage. The stress range reduction in the base SA-302-C compared to that of SA-387-22 is 11.4% for axial stress range and 15.5% for hoop.

6. 2 Conclusion

This study compared ASME approved base and cladding materials applicable for delayed coke drums. The comparison of the materials was based on thermo-mechanical and metallurgical properties and results of two types of Finite Element Analyses. One was the axisymmetric elastic-plastic analysis to examine the stresses in clad during heating-up stage as well the cyclic stress during heating-up and cooling down cycles. Another analysis was the axisymmetric thermo-elastic analysis to examine the stresses in the shell during the quenching stage.

Among the materials studied (Base steels: SA-516-70, SA-387 Grades 11, 12, and 22, SA-204-C, SA-302-C and Cladding Materials: 405, 410, 410S stainless steels and high Nickel alloys N06600 and N06625) SA-302-C base and N06625 clad pair is most suitable for delayed coke drum applications based on the following advantages:

- SA-302-C:
    - Has the highest yield and ultimate strength while maintaining low Young's modulus and comparable ductility to other materials studied.
    - Easier to weld than Chrome-Molybdenum base steels.
    - Higher content of Manganese in SA-302-C is beneficial to reduce hot shortness and creep embrittlement at high temperature.
    - Based on FE Analyses it has the lowest ratio of maximum von Mises stress to yield strength as well as the smallest stress range

under the thermo-mechanical cyclic loading (including water quenching) sceneries experienced by the coke drums.

- N06625:
  - Has the highest yield and ultimate strength while maintaining high ductility.
  - Meets corrosion resistance for delayed coke drum application.
  - Has good match of CTE with SA-302-C base and remains in elastic range during heating-up and quenching stages.
  - Has significantly lower axial and hoop stress ranges compared to use 410S stainless steel as the cladding material.

Thus, the combination of base SA-302-C and clad N06625 is proposed for delayed coke drum application.

RECOMMENDATIONS FOR THE FUTURE WORK

In order to complete material selection process for delayed coke drums it is recommended to perform additional experimental work on base steels SA-387-22 and SA-302-C and cladding materials 410S and N06625.

The recommended experimental work is the following:

- Verify basic mechanical properties of those materials including CTE, yield strength, ultimate strength, and ductility within the temperature range for coke drum applications. Perform fatigue tests of the above materials. Two types fatigue tests need to be performed: fatigue tests under constant temperature (especially at highest temperature for coke drum application) and thermo-mechanical fatigue tests (simultaneous cyclic temperature and mechanical loading).
- Develop suitable fatigue life prediction theory for the materials under thermal-mechanical cyclic loading conditions applicable for coke drum application.

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