

Challenges of Processing Heavy Canadian Crudes

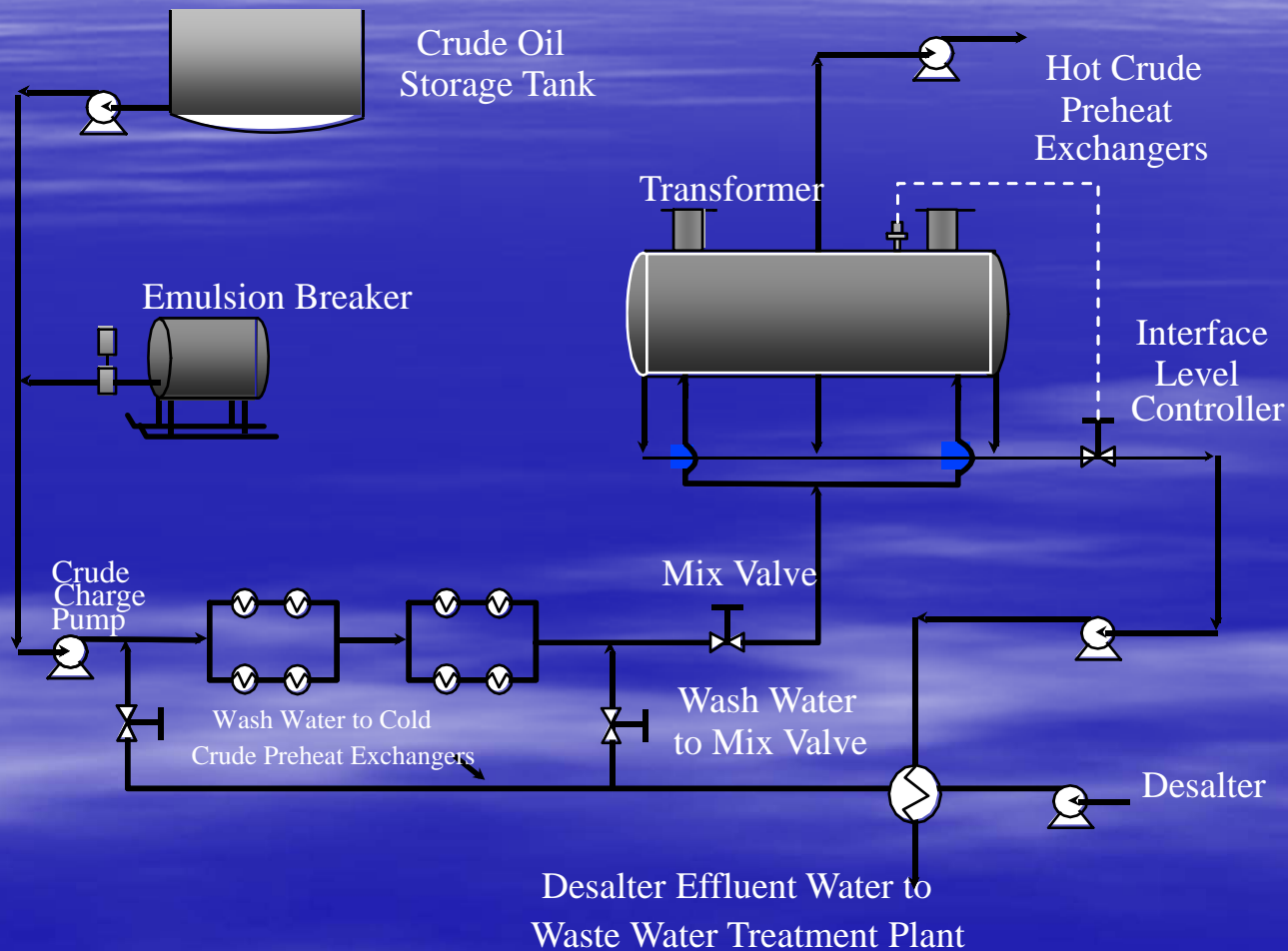
Challenges of Processing Heavy Canadian Crudes

- Single & Two [2] Stage Desalting
 - Consequences of leaving salt in crude
- Solids in Canadian Crudes
 - Impact of solids
- Stream TAN's
 - Why are they different?
- Corrosion Control Methods
 - Dilution
 - Chemicals
 - Metallurgy
- Processing Canadian Crude
 - Point of View
 - ID Effected Circuits
 - Requirements for TAN Corrosion
- Understanding 2nd & 3rd Order Effects

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Simplified Single Stage Desalters

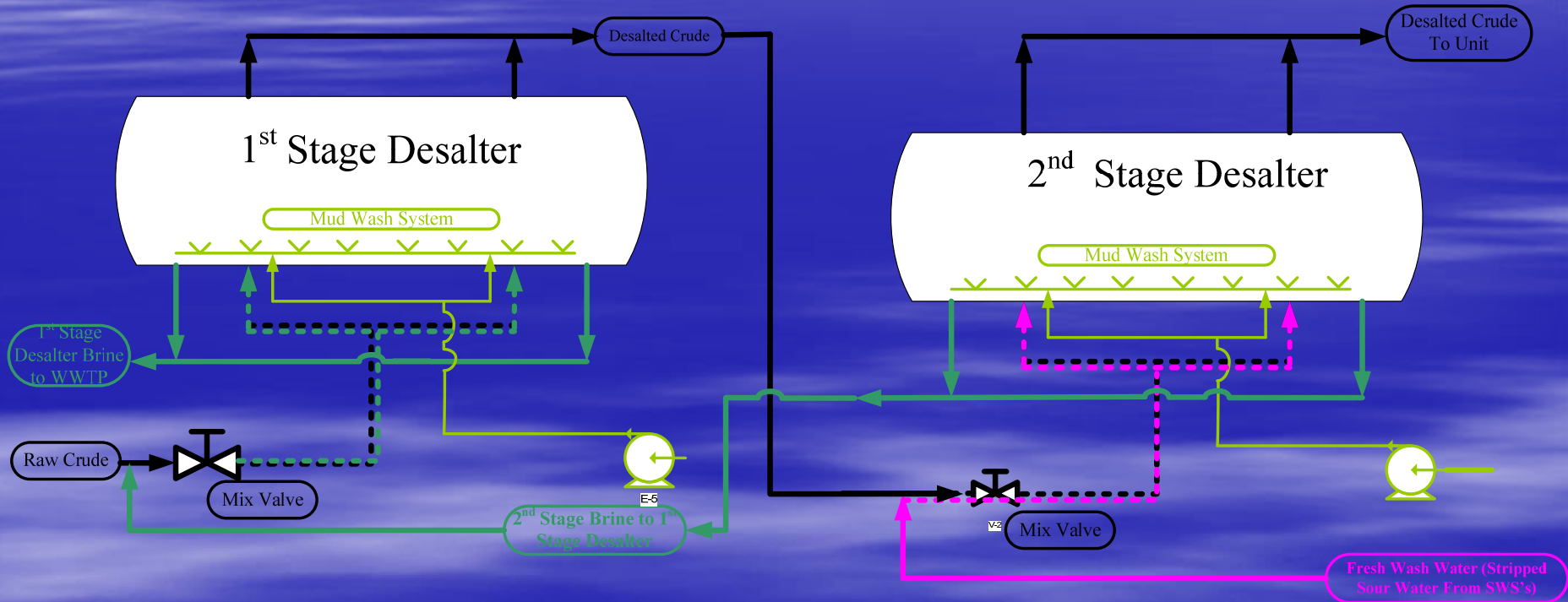
90% Salt removal per stage. Therefore, a typical crude at 40 ptb would desalt to $\sim (.1) \times 40 = 4$ ptb in the 1st Stage.



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What does two Stage Desalting look like?

90% Salt removal per stage. Therefore, a typical crude at 40 ptb would desalt to $\sim (.1)*40= 4$ ptb in the 1st Stage, and $(.1)(.1)40= 0.4$ ptb at the end of the 2nd stage.



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Results of leaving salt in the desalted crude?

- Crude preheat train fouling
- Crude heater fouling
- Vacuum heater fouling
- Duty requirement to vaporize water in the desalted crude
- Caustic usage or increased overhead chlorides/corrosion
- Overhead neutralizer usage

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Results of leaving salt in the desalted crude?

- Coker impact
- Deactivation of Coker Naphtha HDS due to Si
- Chemical/silicone usage
- Units downstream of crude – HCl corrosion issues

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Impact of solids in the desalted crude and solids going to the WWTP

- Negative impact on dehydration
 - Crude preheat train fouling
 - Crude heater fouling
 - Vacuum heater fouling

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Impact of solids in the desalted crude and solids going to the WWTP

- Negative impact on downstream Hydrotreating reactors:
 - Increasing reactor pressure drop
 - Poisoning of reactor catalyst bed
- Stabilize emulsions and increase chemical demand
- Difficult to process solids after they are removed from the water

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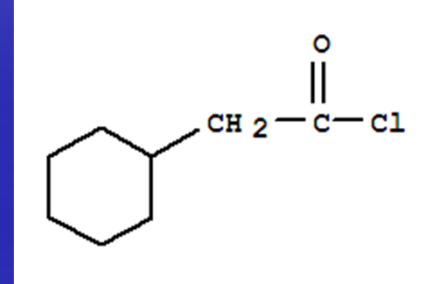
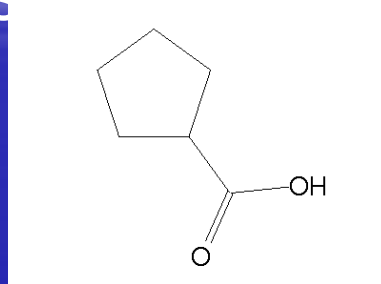
- TAN stands for Total Acid Number
- TAN represent the amount of KOH in mg required to neutralize the acids in one gram of oil.
- ASTM D664 is the most common method for measuring TAN
 - Potentiometric titration in nonaqueous solution
 - The oil is dissolved in a special solvent mixture, consisting of toluene and propanol containing enough water so that the pH electrode can measure a potential.



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What is Naphthenic Acid?

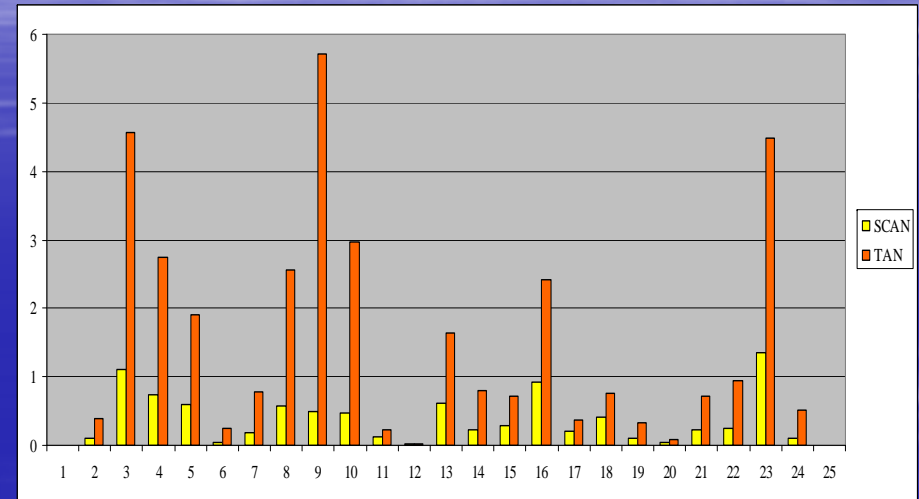
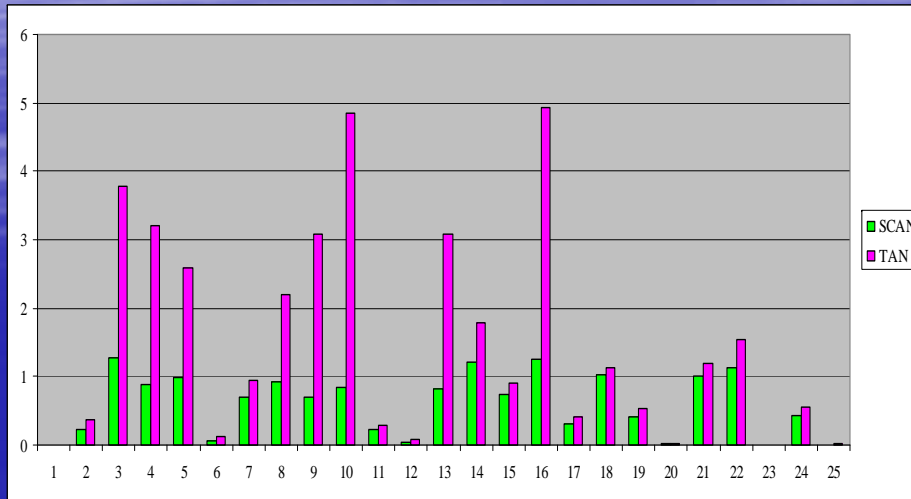
- Naphthenic acid represents a mixture of several cyclopentyl and cyclohexyl carboxylic acids



- Presence in crude oil and are a major contaminant in the oil derived from tar sands.
- Crude oils with a high naphthenic acid content are referred to as “high TAN” crudes

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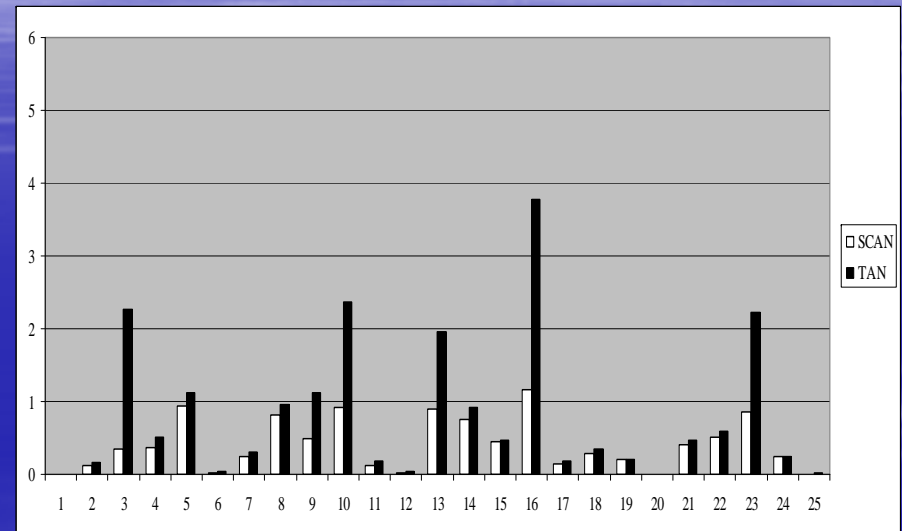
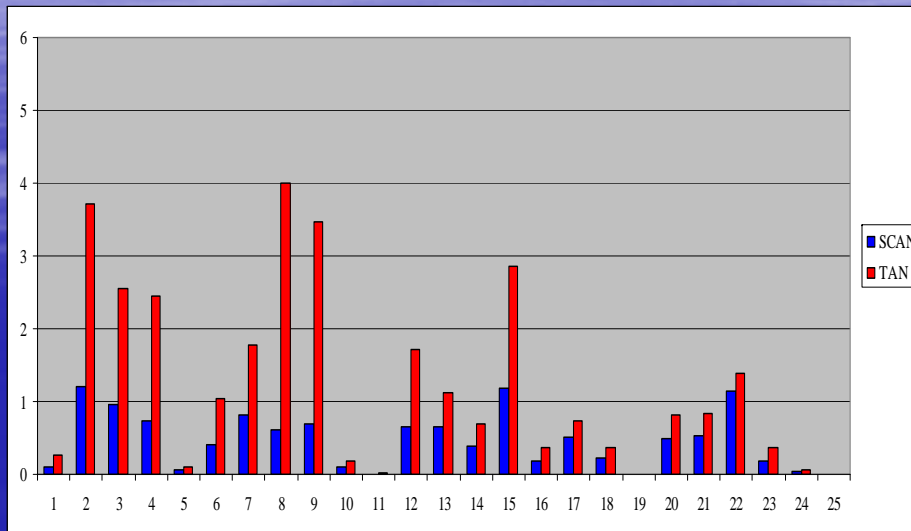
Not All Streams are Created Equal



- Insight into corrosivity versus TAN for fractions and whole crudes is very difficult at best
- Many studies have been undertaken and are underway to characterize the content, structure and corrosivity of high acid crudes and fractions
- Efforts to characterize the content, chemical structure and corrosivity of acids in crudes and their fractions are challenged by:
 - Complexity of the acid mixtures
 - Scarcity of suitable analytical means

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Not All Streams are Created Equal



- Another complication is determining the distribution of naphthenic acids in the different fractions
 - Typically done by analyzing the various fractions from the completed assay
 - Distillation conditions may expose the naphthenic acid in the higher boiling fractions to longer resident times at higher temperatures than what would be seen in the actual unit
 - Because of thermal decomposition, this can lead to lower acid numbers which can lead to underestimating the risk of corrosion

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Corrosion Control Methods

➤ Dilution is the solution

- Blending of lower TAN crudes with higher TAN crudes to meet the desired crude TAN
- Relatively inexpensive
- Can cause fouling and desalter problems
- Not an option for refiner with a single source of crude
- Blending to a “safe” TAN is an uncertain method of control. i.e. tank heel management

➤ Chemicals

- Can reduce corrosion rates by as much as 90%
- All major chemical companies have naphthenic acid corrosion inhibitors [Sulfur or phosphorous]
- Expensive – Low capital expense, significant operating costs. Can be used as a gap closer to get system to material upgrade

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Corrosion Control Methods

➤ Metallurgy

- Most effective long term solution to reducing corrosion rates
- Expensive – Large capital expense
- Unlikely the complete unit would be able to be completed at one time. Phased approach must likely
 - Material availability
 - Shut-down windows are short
 - Complexity
- Can pick the correct alloy for the desired circuit

➤ Other Methods

- Decarboxylation
 - Expensive –significant operating costs
 - Low capital required
 - Generates CO/CO₂ which can lead to addition corrosion issues

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➤ TAN Originates in Crude

➤ Destroyed in either:

- Hydrotreater
- Desulfurizer
- Coke Drums
- FCCU

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➤ **Streams to Build TAN Capability =
Stream with Temp > 450F**

- - #1/2 Fuel Oil
- - LGO
- - Crude/Vacuum
- - LVGO/HVGO
- - VTB

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- Point Of View [POV] - A brief, but; detailed description [TAN, Sulfur, Solids, Salt and Gravity] of the charge for each crude unit
- Limits of operation [TAN, Sulfur] for each circuit [i.e. Whole Crude, Fuel Oils, Heavy & Light Gas Oils, Vacuum Tower Bottoms] that will see TAN and which operates at > 450 °F

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Listing of all equipment which operates at > 450 °F

- Drums
- Towers
- Separators
- Exchangers
- Piping [include control valves]
- Pumps

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Information needed to determine expected life and corrosion rates

- Line or equipment number
- Description
- Service
- Material of construction
- Maximum operating temperatures
- % sulfur range
- Expected TAN range
- Minimum recorded thickness
- Last Inspection date
- Expected corrosion rates
- Remaining Life of existing material

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Line #	Description	Service	Material	Max. Operating Temp. °F	Sulfur (wt%)	Expected TAN @ 2	TAN Range @ 2	Corr. Rate [MPY] @ 2 TAN	Min. T Recorded	Min. T Required Trigger	Last Insp. Date	Lab Data Corr. Rate [MPY]	Rep. Corr. Rate [MPY]	Remaining Life Years (Moral Case) @ 2 TAN	TML Retirement Date @ 2.0 TAN	Comments / Replacement ?????	
2#217 EC	25P-22 A/B to 29022 EC	VTB	9% Cr.	692	5.00%	1.1-2.2	0.7-2.1	10 20	0.180	0.18	05/01/03	5 mpy	64.4	0.0	0.0	07/03	Replace with 317L Clad mat'I Includer 29022EC
2#120 A	25V-4 TO 25V-7	# 2 Fuel Oil	CS	575	2.50%	.7-2.3	.7-4.0	45 90	0.320	0.20	04/01/02	5	19.1	1.3	2.7	0808	Replace with 9% Cr.
2#120 A	25V-4 TO 25V-7	# 2 Fuel Oil	CS	575	2.50%	.7-2.3	.7-4.0	45 90	0.310	0.18	04/01/02	5	19.1	1.4	2.9	0808	Replace with 9% Cr.
2#120 A	25V-4 TO 25V-7	# 2 Fuel Oil	CS	575	2.50%	.7-2.3	.7-4.0	45 90	0.280	0.15	04/01/02	5	19.1	1.4	2.9	0808	no 6" only reducer and CV. Replace with 9% Cr.
2#121 A	2#120 TO 25P-11A/B	# 2 Fuel Oil	CS	575	2.50%	.7-2.3	.7-4.0	45 90	0.280	0.15	05/01/03	5	12.1	1.4	2.9	1/9/05	no 6" only reducer.
2#121 A	2#120 TO 25P-11A/B	# 2 Fuel Oil	CS	575	2.50%	.7-2.3	.7-4.0	45 90	0.320	0.18	05/01/03	5	12.1	1.6	3.1	0808	Replace with 9% Cr. - P&ID says reducer is 12"
2#121 A	2#120 TO 25P-11A/B	# 2 Fuel Oil	CS	575	2.50%	.7-2.3	.7-4.0	45 90	0.322	0.18	05/01/03	5	12.1	1.6	3.2	0808	
2#139 C	25V-7 TO 25 P 10A/B	# 2 Fuel Oil	CS	540	2.50%	.7-2.3	.7-4.0	30 60	0.237	0.13	01/01/01	5	3.1	1.8	3.6	0808	Reducer. Replace with 9% Cr.
2#131 A	25V-7 TO 25V-4	# 2 Fuel Oil	CS	575	2.50%	.7-2.3	.7-4.0	45 90	0.360	0.18	02/01/04	5	1.3	2.0	4.0	0808	Replace with 9% Cr.
2#140 C	25 P 10A/B TO 25E-7 SS	# 2 Fuel Oil	CS	540	2.50%	.7-2.3	.7-4.0	30 60	0.270	0.15	01/01/01	5	7.8	2.0	4.0	1/1/03	Replace with 9% Cr.
2#216 EC	25V-15 to 25P-22 A/B	VTB	9% Cr.	692	5.00%	1.1-2.2	0.7-2.1	10 20	0.260	0.22	05/01/03	5 mpy	38.2	2.0	4.0	0808	Replace with 317L Clad mat'I
2#222 EC	29022 EC to 25E-15 E/F/TS	VTB	9% Cr.	692	5.00%	1.1-2.2	0.7-2.1	10 20	0.220	0.18	03/01/04		20.5	2.0	4.0	3/1/06	Replace with 317L Clad mat'I

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Understanding 2nd and 3rd Order Effects

➤ TAN comes with the crude and is only destroyed at certain locations:

- Hydrotreater/ desulfurizer reactors
- FCCU reactors
- Coker reactors

➤ The same system that was used for the front end of the refinery [i.e. crude/vacuum units] must now be completed for each unit:

- Process streams that will see temperatures >450°F

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Questions