



Organic Chloride - the Threat and the Challenge!

De-Yuan Fan

Westhollow Technology Center

Shell Global Solutions US, Inc.

Houston, Texas

June 2007



Our far sight ...

"I don't think anybody anticipated the breach of the levees. They did appreciate a serious storm but these levees got breached and as a result much of New Orleans is flooded and now we're having to deal with it and will."

G. W. Bush, September 1, 2005
on ABC's "Good Morning America" after Hurricane Katrina

Do you have an **Effective** Prevention Program in place for a strike by...

Organic Chlorides?

Non-Extractable Chlorides?

Non-Desaltable Halogens?(NDH)

Phantom Klorida?



In this Presentation

- The Threat (Risk)
 - Recognizing the Threat
 - Understanding the Threat
 - Communicating the Threat
- The Challenge (Prevention)
 - Practical
 - Cost Effective
- What we should do
 - Next step(s)

Recognizing the Risk

- The risk of NDH is well recognized by the technical community:
 - 1960's – initially reported by K. Brooks
 - 1970's – 80's – multiple incidents reported in the industry
 - 1990's – Several major incidents in US, EU, and Asia
 - 2000 – Major fire in a gulf coast refinery
 - 2001 – STG 34 formed an ad-hoc “organic chloride” discussion group
 - 2002 – NACE MP published an article on “Phantom Chlorides”
 - 2005 – STG 274 completes the TCR – the very first industry document
- The risk of NDH is not fully appreciated by the industry management, possibly by the following perceptions:
 - The likelihood of occurrence is very low – “it won't hit me!”
 - The consequence is not very high – “I can always manage!”
 - The cost of mitigating the problems is too high – “I cannot afford it!”

Understanding the Threat

- Risk = Likelihood x Consequence
- Annual Likelihood of NDH Occurrence:
(Conservative Estimates based upon reported incidents in the refining industry)
 - In the entire refining industry in the US and Canada
 - 1/10
 - In a major refining company
 - 1/100
 - In a specific refinery
 - 1/1000
 - In a specific unit/equipment
 - 1/10,000

Understanding the Threat, cont'd

- Consequence
 - Units & Equipment affected
 - Crude overhead system and NHT feed/effluent system
 - Exchanger shells and tube bundles
 - Other side cuts (e.g. Kerosene.) and downstream units
 - Corrosion
 - Rates: 1000 – 5000 mpy (3 – 14 mils/day)
 - Thru-wall failure of BWG 12 in 8 days and 4" sch. 40 pipe in 17 days
 - Corrosion morphology and failure scenario
 - Pitting - pinhole – flammable light hydrocarbon
 - Thinning - rupture – sudden & catastrophic – Fire/VCE
 - Significant loss of business and HS&E impact

Communicating the Threat – Risk

Unit Value (< 2 weeks)	\$250,000	per day
Unit Value (> 2 weeks)	\$1,000,000	per day

		Probability	Consequence	Risk
Refiner!	0.01 NDH	0.05	Leak - no fire	4.50E-04 \$ 20,000,000 \$ 8,999
	0.8999 Not find w/inspection	0.85	Leak - fire	7.65E-03 \$ 19,700,000 \$ 150,688
		0.10	Major loss of containment	9.00E-04 \$269,500,000 \$ 242,523
		0.90	Shutdown	9.0E-07 \$ 19,600,000 \$ 18
	0.0001 Find w/inspection	0.10	Slowdown & Repair	1.0E-07 \$ 3,950,000 \$ 0.40
	0.001 Detected in Logistics	1.00	Preventive Action	1.0E-05 \$ 1,000,000 \$ 10.00
		0.50	Preventive Action	5.0E-04 \$ 1,000,000 \$ 500.00
	0.10 Detected in Units	0.50	Slow Response (<u>Leak</u>)	5.0E-04 \$ 44,695,000 \$22,347.50
	0.99 No NDH	-	No Consequence	0.99 \$ - \$ -

Base Case – do nothing!

1.0000	Annual Risk	\$ 425,086
	Risk in 5 Yrs	2,125,429
	Risk in 10 yrs	4,250,858

Risk reduction - Good Monitoring Practices

Unit Value (< 2 weeks) =	\$250,000	per day
Unit Value (> 2 weeks) =	\$1,000,000	per day

		Probability	Consequence	Risk	
Refiner!	0.01 NDH	0.05 Leak - no fire	5.00E-05 \$ 20,000,000	\$ 999	
		0.0999 Not find w/inspection			
		0.85 Leak - fire	8.49E-04 \$ 19,700,000	\$ 16,728	
		0.10 Major loss of containment	9.99E-05 \$269,500,000	\$ 26,923	
		0.90 Shutdown	9.0E-07 \$ 19,600,000	\$ 18	
		0.0001 Find w/inspection	0.10 Slowdown & Repair	1.0E-07 \$ 3,950,000	\$ 0.40
		0.001 Detected in Logistics	1.00 Preventive Action Taken	1.0E-05 \$ 1,000,000	\$ 10
		0.90 Detected in Units	0.90 Preventive Action Taken	8.1E-03 \$ 1,000,000	\$ 8,100
			0.10 Slow Response (Leak)	9.0E-04 \$ 44,695,000	\$ 40,226
		0.99 No NDH	- No Consequence	0.99 \$ -	\$ -

1.0000	Annual Risk	\$ 93,004
	Risk in 5 Yrs	465,019
	Risk in 10 yrs	930,038

Risk reduction of BEST monitoring practices

Unit Value (< 2 weeks) = \$250,000 per day
 Unit Value (> 2 weeks) = \$1,000,000 per day

				Probability	Consequence	Risk	
Refiner!	0.01 NDH	0.0099 Not find w/inspection	0.05 Leak - no fire	4.95E-06	\$ 20,000,000	\$ 99	
			0.85 Leak - fire	8.42E-05	\$ 19,700,000	\$ 1,658	
			0.10 Major loss of containment	9.90E-06	\$269,500,000	\$ 2,668	
		0.0001 Find w/inspection	0.90 Shutdown	9.0E-07	\$ 19,600,000	\$ 18	
			0.10 Slowdown & Repair	1.0E-07	\$ 3,950,000	\$ 0.40	
			0.001 Detected in Logistics	1.00 Preventive Action Taken	1.0E-05	\$ 1,000,000	\$ 10
		0.99	Detected in Units	0.99 Preventive Action Taken	9.8E-03	\$ 1,000,000	\$ 9,801
				0.01 Slow Response (Leak)	9.9E-05	\$ 44,695,000	\$ 4,425
		0.99 No NDH	-	No Consequence	0.99	\$ -	\$ -

1.0000	Annual Risk	\$ 18,679
	Risk in 5 Yrs	93,393
	Risk in 10 yrs	186,786

Prevention Options (NACE Publ 34105)

- **Source Control – Production Facilities**
 - Contribution to the NDH sources (~30%?)
 - **Obstacles** (see Kapusta paper, Corr/03649 on OFC)
 - A large number of chemicals in use and being formulated
 - A global crude market with hundreds of crudes
 - Poor communication between refiners and producers
 - No industry standards and recommended practices
 - **Activities and Opportunities**
 - CCQTA – Canadian Crude Quality Technical Association
 - COQG – Crude Oil Quality Group (in the US)
 - NACE – STG 34 – refining group only
 - API - ?
 - **Effort and Cost**
 - Participation and funding of cooperative industry projects
 - A comprehensive program to manage oil field chemicals
 - **Ready for Implementation**
 - 10+ years

Prevention Options, cont'd

- Source Control – Transportation (Pipeline and Tankers)
 - Contribution to the NDH sources (~50%?)
 - Obstacles (see Gutzeit paper, Corr/0694 and comments to TG 274)
 - Complex logistics - multiple possible entry points for contamination
 - A large number of pipeline and shipping companies involved
 - Long turnaround time for NDH analysis in crude oil
 - Frequent sampling and analysis required
 - Poor communication between refiners and transportation providers
 - No industry standards and recommended practices
 - Activities and Opportunities
 - CCQTA and COQG programs
 - NACE – STG 34 – TG274 – no pipeline involvement
 - API - ?
 - Effort and Cost
 - Participation and funding of cooperative industry projects
 - A comprehensive program to manage all potential contamination sources
 - Sample collection and chemical analysis (by owner/operator of pipeline)

Prevention Options, cont'd

- Source Control – Logistics inside refinery
 - Includes crude storage and blending, reruns (refinery & chemical), purchased intermediate feeds, and cross-unit transfers
 - Contribution to the NDH Prevention (~20%?)
 - Obstacles
 - Short lead time as a result of low storage capacity
 - Long turnaround time for NDH analysis in crude oil
 - Very frequent sampling and chemical analysis required
 - Activities and Opportunities
 - CCQTA and COQG programs
 - NACE – STG 34 – TG274 – no pipeline involvement
 - API - ?
 - Effort and Cost
 - Participation and funding of cooperative projects
 - Sample collection, retention, and analysis (equipment and labor)
 - Ready for Implementation
 - 2-5 years

Prevention Options, cont'd

- Process Monitoring and Control
 - Establish **preset limit(s)** and actively monitor the following process parameters:
 - Chlorides and pH in crude overhead boot water
 - Crude overhead corrosion rate (via online, real-time system)
 - NHT effluent pressure drop
 - NHT feed/effluent exchanger temperature profile and heat transfer
 - Chlorides in NHT separator water
 - Total chlorides in NHT feed
 - Establish **predetermined responses**
 - Verify the measurements to confirm data quality
 - Communicate the threat to all involved parties
 - Take decisive actions to identify and isolate sources
 - Secure unit operations and/or prepare to shut the unit down
 - Conduct followup inspections

Prevention Options, cont'd

- Process Monitoring and Control
 - Obstacles
 - Damage already occurring when detected/confirmed
 - Very short response time required (a few days?)
 - Complacency after months and years of no activity
 - Potential over-reaction due to periodic false alarms
 - Effort and Cost
 - A well established set of monitoring systems with realistic limits
 - A robust and efficient alarm and alert system
 - Chemical analysis staff and equipment
 - Ready for Implementation
 - 0-1 year(s)
 -

What should be out next step?

Questions, Comments, Suggestions?