The Challenge of Risk Control in a Hydrogen based Economy, Part II

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Chemical Risk Management

What are the risks, how can we determine them,
How can we avoid, how to reduce, when can we be satisfied?

Summer School UofU
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Hazard Identifation:

- Process Safety Studies/ Tests/ stability, ignitability
- Check list: Amounts, site, properties, equipment, process, safety systems, quality management........etc.
- HAZard and OPerability study: HAZOP
- *Dow Fire & Explosion Index*
- *FACTS, MHIDAS, MARS* incident data banks
- FMECA: Failure Mode, Effect and Criticality Analysis
- Delphi methods: Brainstorming
- Bayesian influence network: Systemic
- Cause tree: PLANOP

Class 1 Index method

National Fire Protection Agency (NFPA) rating system for Flammability (N_f), Reactivity (N_r) and Health (N_h).

Flammability (f)	NFPA Rating (N_f)	Reactivity (r)	NFPA Rating (N_r)	Health (h)	NFPA Rating (N_h)
Non-combustible	0	Non-reactive, even under fire	0	No hazard beyond that of ordinary combustibles	0
Flash point >100 ^oC	1	Mildly reactive, upon heating and pressure	1	Only minor injury likely	1
40^o < flash point < 100 ^oC	2	Significantly reactive without heating	2	Medical attention required to avoid temporary or residual injury	2
20^o < flash point < 40 ^oC	3	Detonation possible with confinement	3	Materials causing serious injury	3
Flash point < 20 ^oC	4	Detonation possible without confinement	4	Short exposure causes death or serious injury	4

Dow Fire & Explosion Index: penalties and credit points

FIRE & EXPLOSION INDEX

DOW

AREA / COUNTRY	DIVISION	LOCATION	DATE
SITE	MANUFACTURING UNIT	PROCESS UNIT	
PREPARED BY:	APPROVED BY: (Superintendent)	BUILDING	
REVIEWED BY: (Management)	REVIEWED BY: (Technology Center)	REVIEWED BY: (Safety & Loss Prevention)	
MATERIALS IN PROCESS UNIT			
STATE OF OPERATION __ DESIGN __ START UP __ NORMAL OPERATION __ SHUTDOWN		BASIC MATERIAL(S) FOR MATERIAL FACTOR	

MATERIAL FACTOR (See Table 1 or Appendices A or B) Note requirements when unit temperature over 140 °F (60 °C)

1. General Process Hazards	Penalty Factor Range	Penalty Factor Used(1)
Base Factor	1.00	1.00
A. Exothermic Chemical Reactions	0.30 to 1.25	
B. Endothermic Processes	0.20 to 0.40	
C. Material Handling and Transfer	0.25 to 1.05	
D. Enclosed or Indoor Process Units	0.25 to 0.90	
E. Access	0.20 to 0.35	
F. Drainage and Spill Control ________ gal or cu.m.	0.25 to 0.50	
General Process Hazards Factor (F_1)		
2. Special Process Hazards		
Base Factor	1.00	1.00
A. Toxic Material(s)	0.20 to 0.80	
B. Sub-Atmospheric Pressure (< 500 mm Hg)	0.50	
C. Operation In or Near Flammable Range ___ Inerted ___ Not Inerted		
1. Tank Farms Storage Flammable Liquids	0.50	
2. Process Upset or Purge Failure	0.30	
3. Always in Flammable Range	0.80	
D. Dust Explosion (See Table 3)	0.25 to 2.00	
E. Pressure (See Figure 2) Operating Pressure ______ psig or kPa gauge; Relief Setting ______ psig or kPa gauge		
F. Low Temperature	0.20 to 0.30	
G. Quantity of Flammable/Unstable Material: Quantity _____ lb or kg; H_C = _____ BTU/lb or kcal/kg		
1. Liquids or Gases in Process (See Figure 3)		
2. Liquids or Gases in Storage (See Figure 4)		
3. Combustible Solids in Storage, Dust in Process (See Figure 5)		
H. Corrosion and Erosion	0.10 to 0.75	
I. Leakage – Joints and Packing	0.10 to 1.50	
J. Use of Fired Equipment (See Figure 6)		
K. Hot Oil Heat Exchange System (See Table 5)	0.15 to 1.15	
L. Rotating Equipment	0.50	
Special Process Hazards Factor (F_2)		
Process Unit Hazards Factor (F_1 x F_2) = F_3		
Fire and Explosion Index (F_3 x MF = F&EI)		

(1) For no penalty use 0.00.

FLASH POINT °C	$H_{comb.}$ x volatility (kJ / mol) bar	FLAMMABILITY N_f \ N_r	0	1	2	3	4
		ADIABATIC DECOMPOSITION TEMPERATURE, T_d K	< 830	830 - 935	935 - 1010	1010 - 1080	> 1080
			REACTIVITY				
none	$< 4 \times 10^{-5}$	0	0	14	24	29	40
> 100	4×10^{-5} - 2.5	1	4	14	24	29	40
40-100	2.5 - 40	2	10	14	24	29	40
-20 - 40	40 - 600	3	16	16	24	29	40
< - 20	> 600	4	21	21	24	29	40
			MATERIAL FACTOR (MF)				

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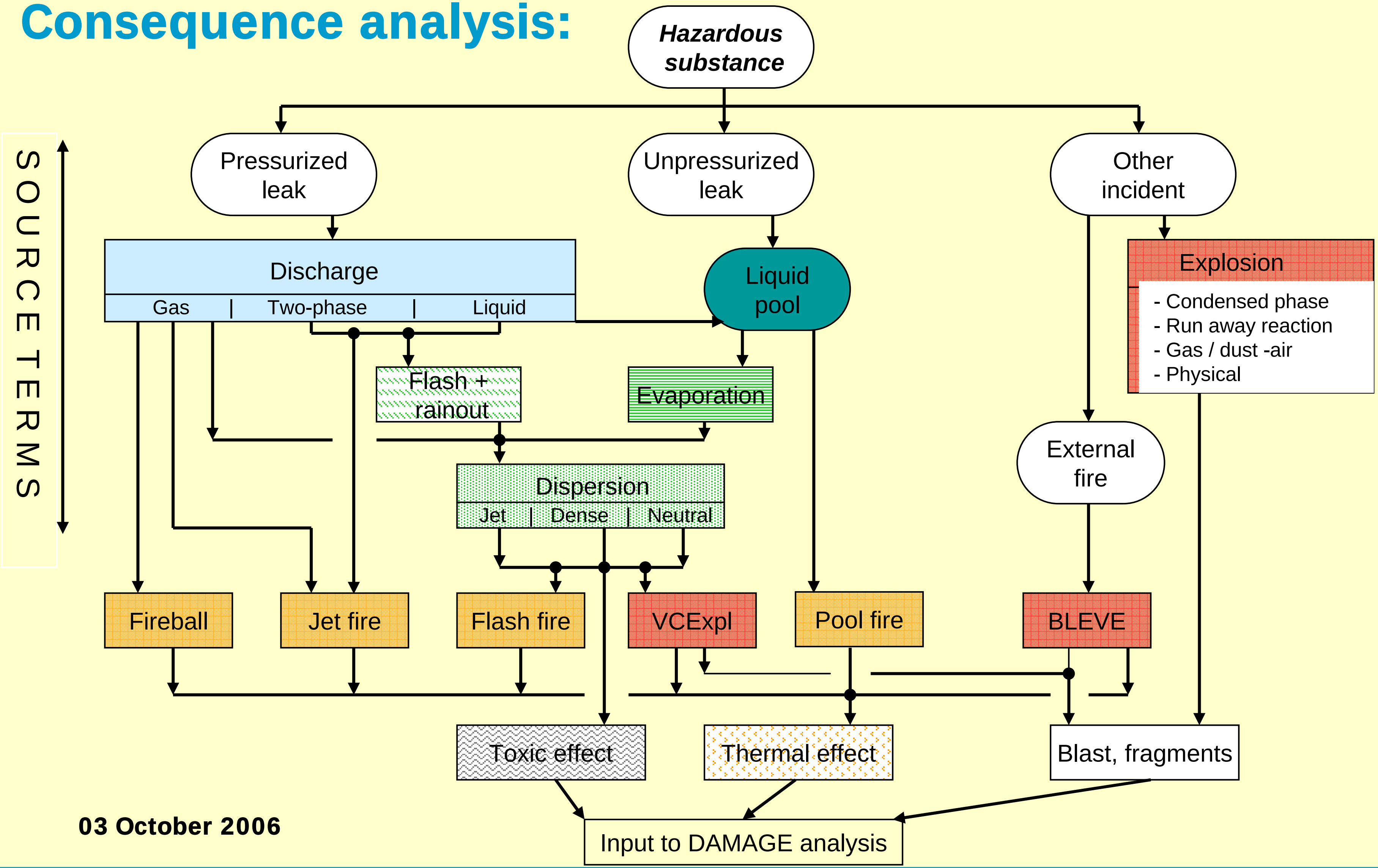
Consequence analysis:



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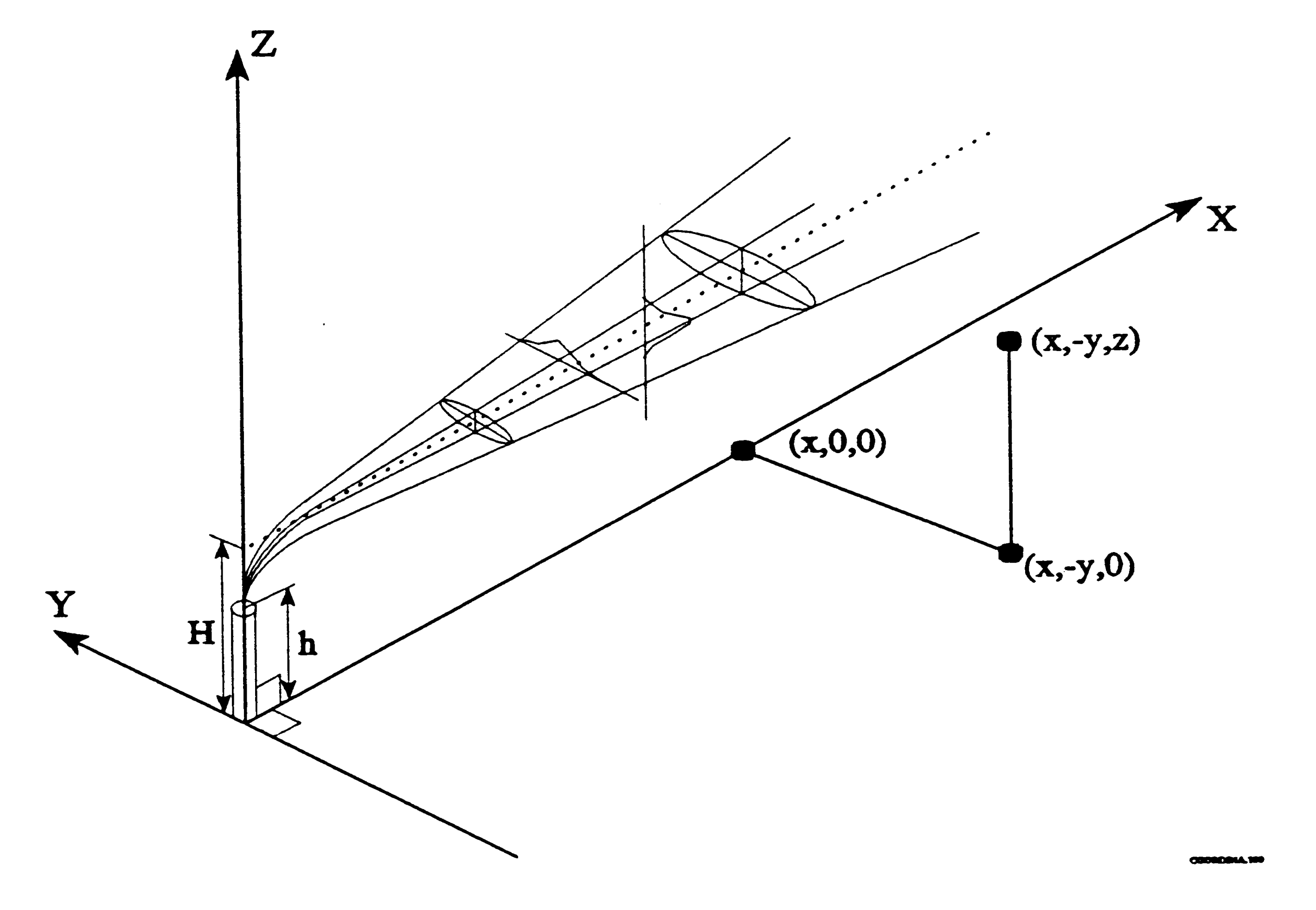
Release models : Yellow Book

- Outflow compressed gas / vapour
- Pressurised liquefied gases: superheated liquid; 2-phase flow : *Boiling Liquid Expanding Vapour Explosion*
- Outflow of liquids
- Evaporation from a boiling liquid pool on land
- Idem from water; rapid phase transition (LNG, LH2?)
- Evaporation non-boiling liquid
- Pool spreading

Gaussian Plume Model:

coordinate system; wind direction is along X-axis



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Gaussian Plume Model

Continuous release:

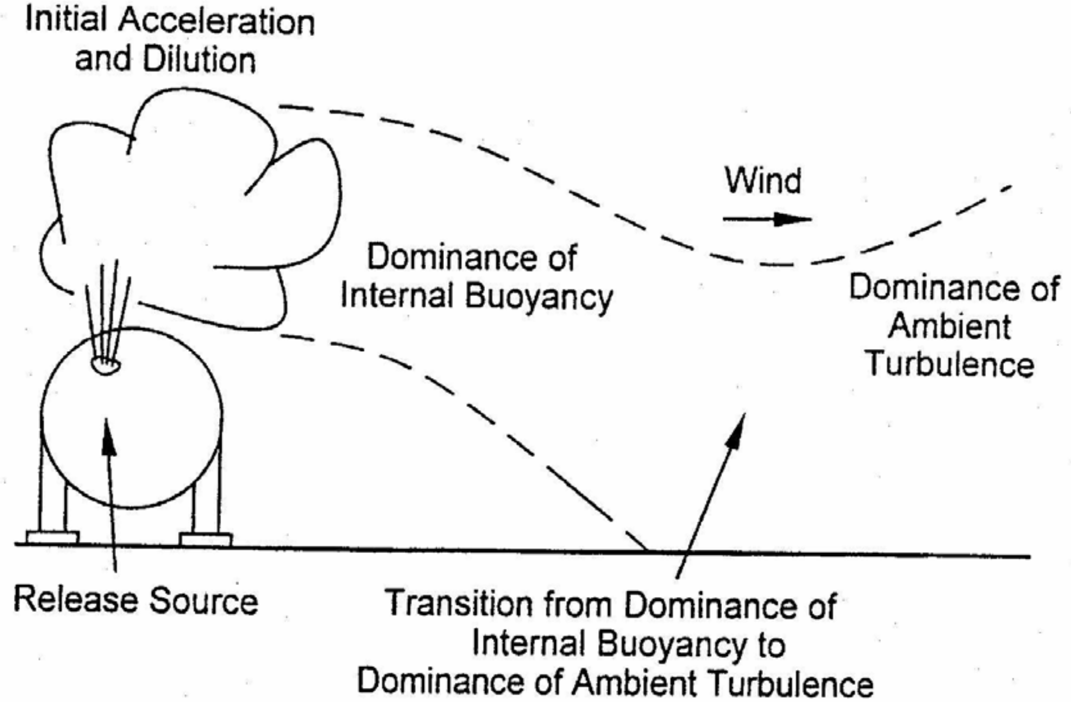
$$C_{x,y,z} = \frac{q}{2\pi\, u\, \sigma_y\, \sigma_z} \exp(-y^2/\, 2\sigma_y^2)\cdot[\exp\{-(z-H)^2/\, 2\sigma_y^2\} + \exp\{-(z+H)^2/\, 2\sigma_z^2\}]$$

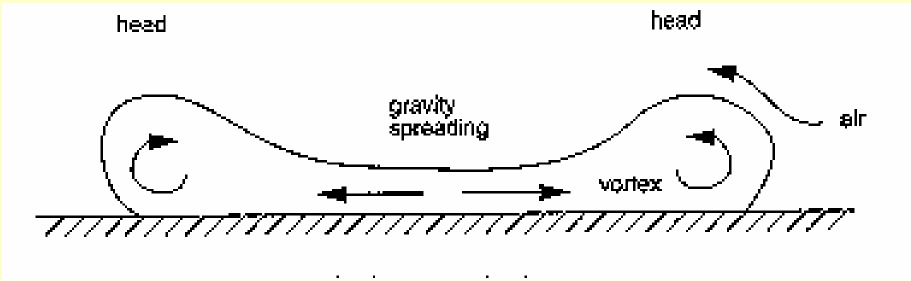
$C_{x,y,z}$	= average concentration at the point x, y, z [kg/m^3];
x	= distance [m] in the average wind direction (x-direction) from point x to the emission source;
y	= horizontal distance [m] from the point x, y, z to the emission source, in a direction (y-direction) horizontal to the average wind direction;
z	= distance [m] from the point x, y, z to the surface of the earth;
q	= intensity of the emission source [kg/s];
u	= average wind speed [m/s] (in x-direction) at the height (H) of the emission source;
σ_y	= dispersion coefficient (or standard deviation) [m] in horizontal direction, perpendicular to the plume;
σ_z	= dispersion coefficient [m] in vertical direction, perpendicular to the plume;
H	= effective emission height (the sum of stack or source height (h) and rise of plume (Δh)) [m];

Instantaneous spill:

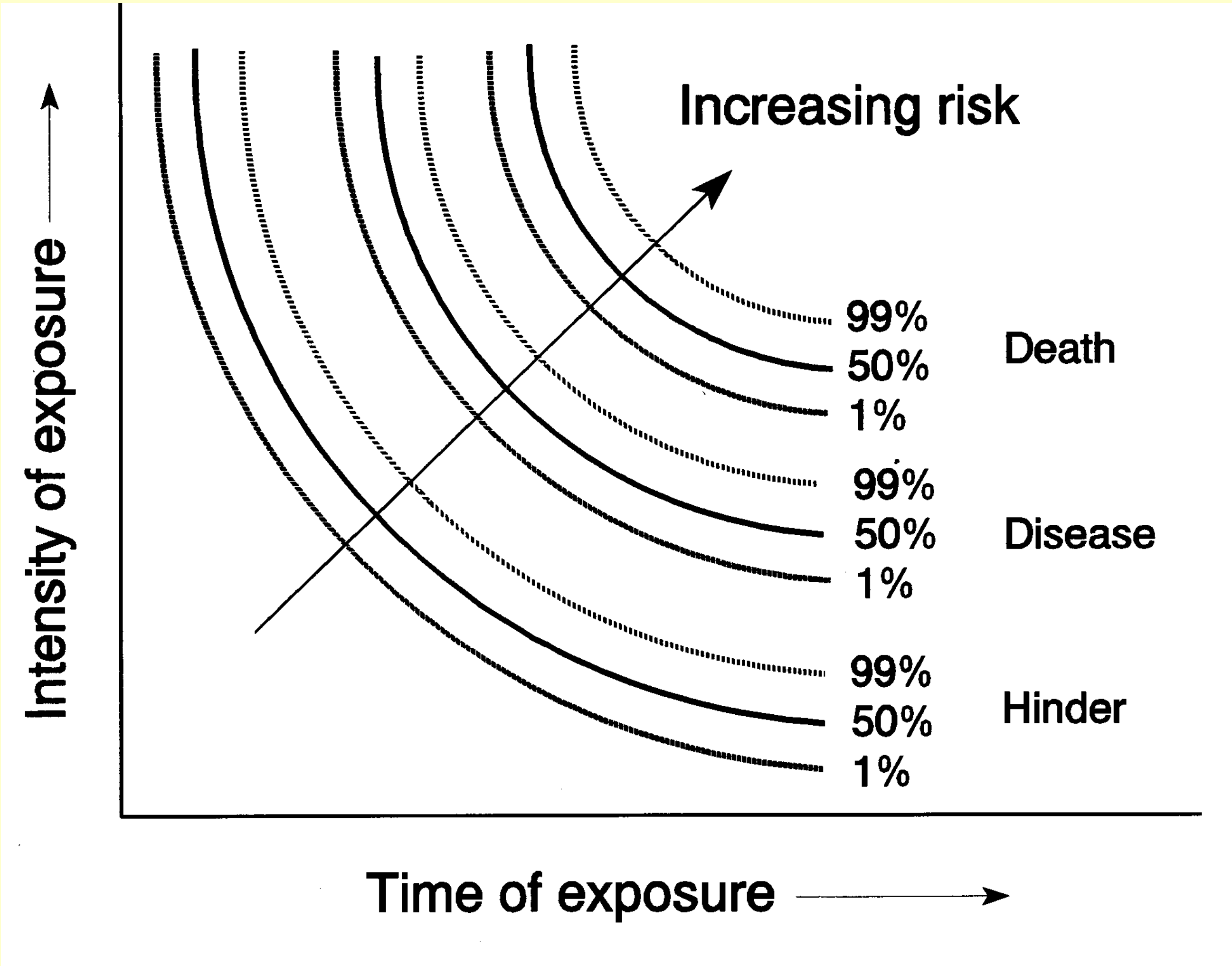
$$C_{x,y,z,t} = \frac{m}{(2\pi)^{3/2}\, \sigma_x\, \sigma_y\, \sigma_z} \exp\{-(x-u\,t)^2/\, 2\sigma_x^2\}\cdot\exp(-y^2/\, 2\sigma_y^2)\cdot[\exp\{-(z-H)^2/\, 2\sigma_z^2\} + \exp\{-(z+H)^2/\, 2\sigma_z^2\}]$$

Gravity slump denser-than-air cloud





Vulnerability: General Model

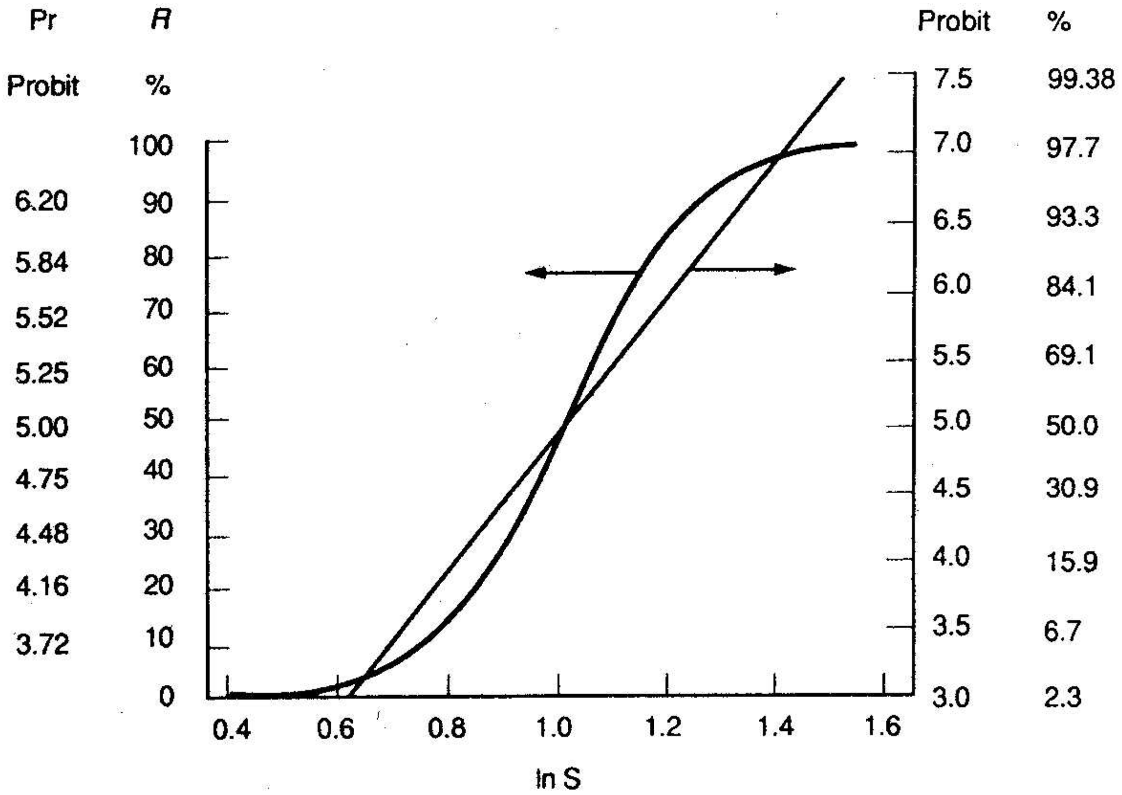


Probit function: $Pr = k_1 + k_2 \ln V$

***Pr* = % vulnerable resource; *V* causative exposure, *f(I, t)*;**

k_1 and k_2 are regression coefficients for:

Heat radiation, blast overpressure, toxic load



Transformation from typical S-shaped Gaussian cumulative distribution function to straight line via:

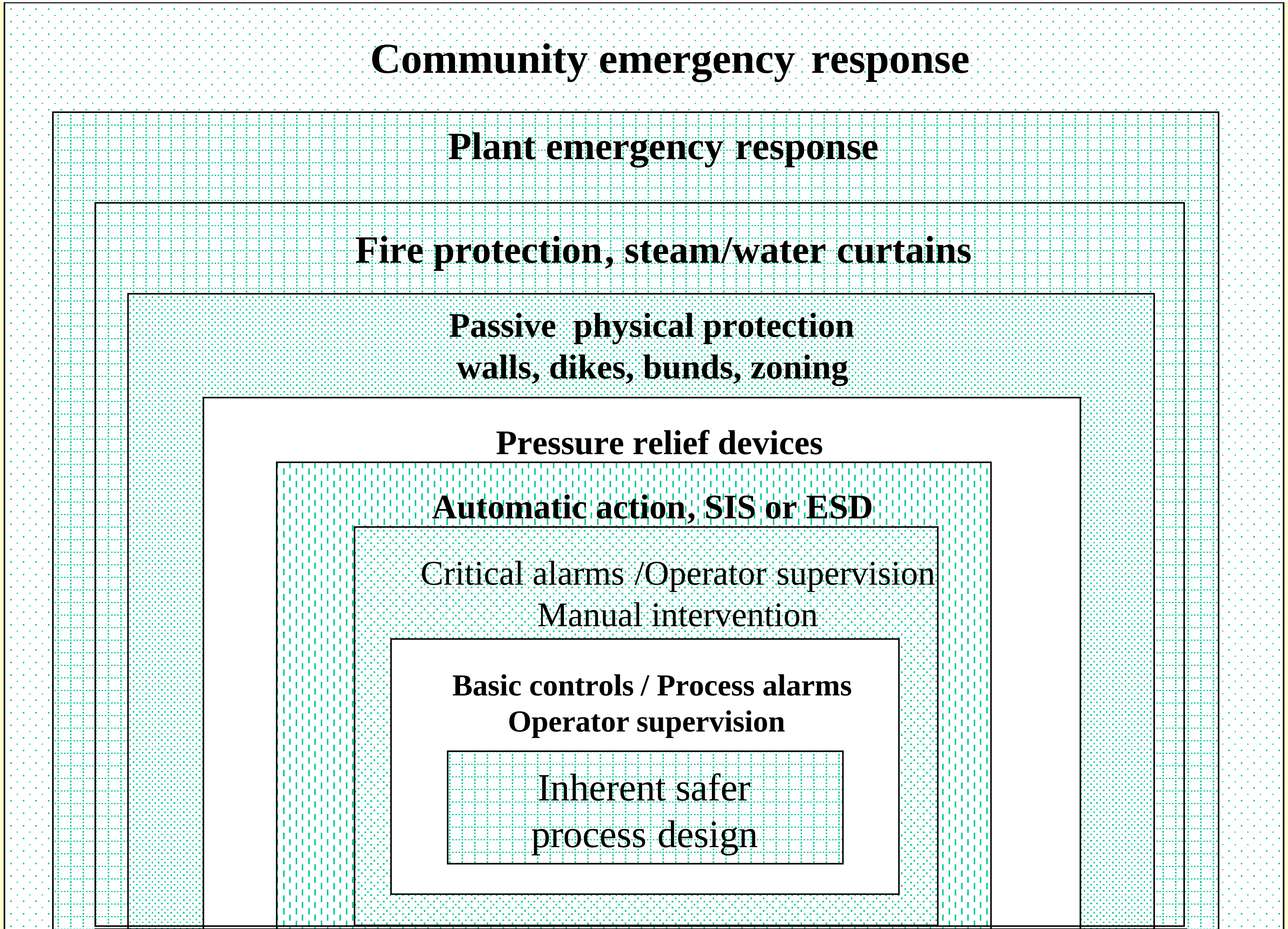
$$R = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\mathrm{Pr}-5} \exp(-u^2/2) \cdot du$$

Why? Because scattered measuring points can then be fitted easily.

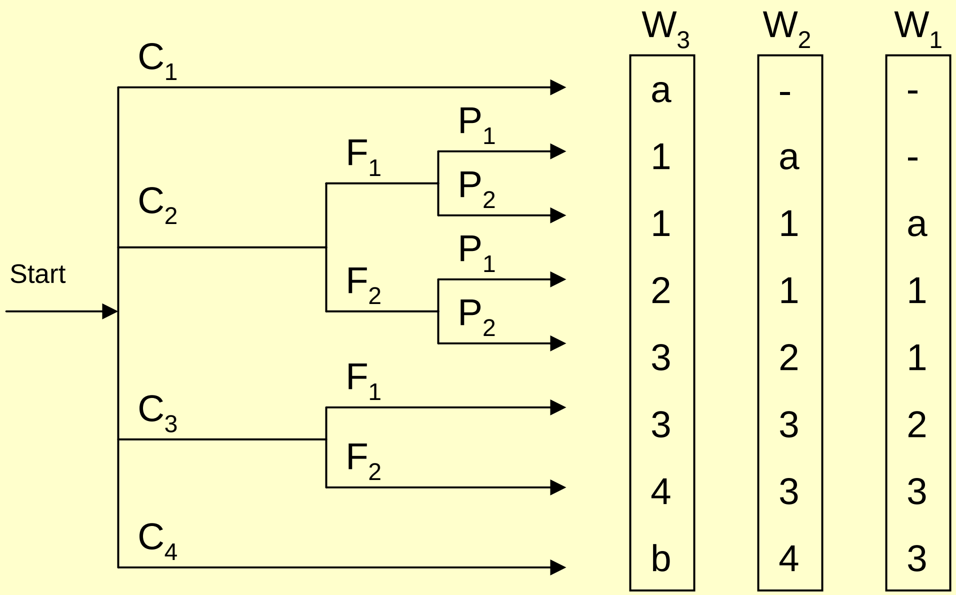
Failure rate data, λ, exponential distribution

$$R(t) = \exp(-\lambda t)$$

Failure rates of equipment	**Catastrophic Freq. [yr^{-1}]**	**Continuous Freq. [yr^{-1}]**	**Leak Freq. [yr^{-1}]**
Atmospheric storage tanks:			
Single containment tank; process or reactor vessel	5×10^{-6}	5×10^{-6}	1×10^{-4}
Tank with protective outer shell	5×10^{-7}	5×10^{-7}	1×10^{-4}
Double containment tank	1.25×10^{-8}	1.25×10^{-8}	1×10^{-4}
Full containment tank	1×10^{-8}		
Pressurised storage tanks:	5×10^{-7}	5×10^{-7}	
Pressure vessel	5×10^{-7}	5×10^{-7}	1×10^{-5}
Pipe work:			
Diameter pipe between 75 and 150 mm	3×10^{-7} /m		2×10^{-6} /m
< 75 mm	10^{-6} /m		5×10^{-6} /m
> 150 mm	10^{-7} /m		5×10^{-7} /m
Pumps:			
Pumps without additional provisions	1×10^{-4}		5×10^{-4}
Pumps with a wrought steel containment	5×10^{-5}		2.5×10^{-4}
Canned pumps	1×10^{-5}		5×10^{-5}
Heat exchangers:			
Dangerous substance outside pipes	5×10^{-5}	5×10^{-5}	1×10^{-3}
Dangerous substance inside pipes, design pressure outer shell < dangerous substance	1×10^{-5}	1×10^{-3}	1×10^{-2}
Dangerous substance inside pipes, design pressure outer shell > dangerous substance	1×10^{-6}		



Independent Layers of Protection "Onion"



IEC 61508 Risk Graph Scheme for minimum risk reduction (abridged)

Legenda:

- = No safety requirement

a = No special safety requirement

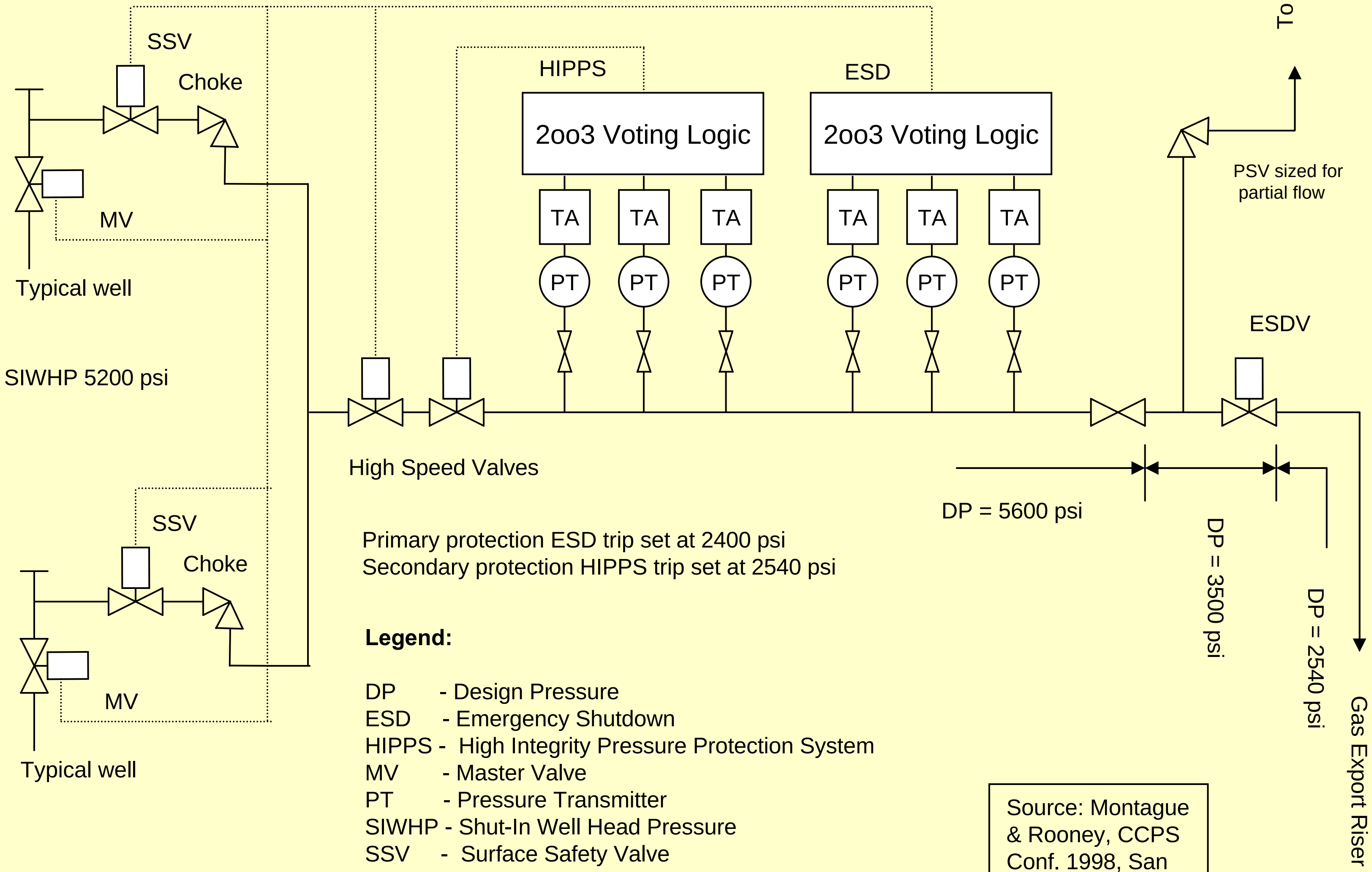
b = A single E/E/PES is not sufficient

1, 2, 3, 4 = Safety integrity level

Risk parameter		**Classification**
Consequence (C)	C1	Minor injury
	C2	Serious permanent injury to one or more persons; death to one person.
	C3	Death to several persons
	C4	Very many people killed
Frequency of, and exposure time in hazardous zone (F)	F1	Rare to more often exposure in the hazardous zone
	F2	Frequent to permanent exposure in the hazardous zone
Possibility of avoiding the hazardous event (P)	P1	Possible under certain conditions
	P2	Almost impossible
Probability of the unwanted occurrence (W)	W1	A very slight probability that the unwanted occurrences will come to pass and only a few unwanted occurrences are likely
	W2	A slight probability etc.and a few unwanted occurrences are likely
	W3	A relatively high probability etc, and frequent etc.

Notes: Other classification schemes would need to be developed for environmental and other material damage.
W is estimated not including SIS; in case no experience exists worst case prediction shall be made.

HIPPS example for an offshore satellite gas platform



Primary protection ESD trip set at 2400 psi
Secondary protection HIPPS trip set at 2540 psi

Legend:

DP - Design Pressure
ESD - Emergency Shutdown
HIPPS - High Integrity Pressure Protection System
MV - Master Valve
PT - Pressure Transmitter
SIWHP - Shut-In Well Head Pressure
SSV - Surface Safety Valve
TA - Trip Amplifier
2oo3 - 2 out of 3

Source: Montague & Rooney, CCPS Conf. 1998, San Antonio, TX

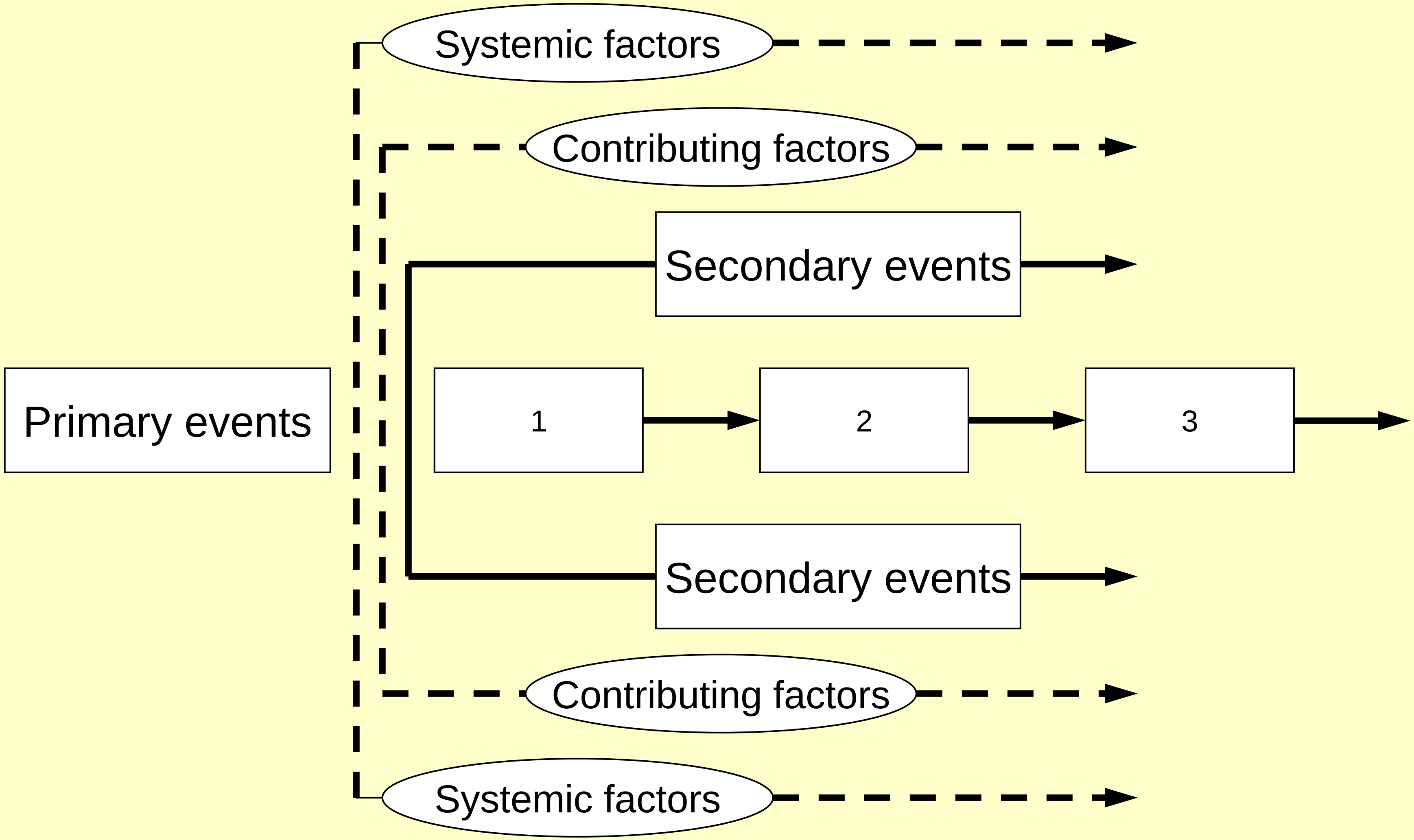
Accident investigation scene :

- Scene of accident investigation: CHAOS!
- As an investigator one has to deal with:

  Fire brigade, police, rumours, emotions, who is to blame, media, witnesses, pictures and sample taking, criminal investigation, no admission, opposing views, shifting around of "Black Peter", who will be paying, liability charges, lawyers, resume of operation, clearing debris, withdrawal of licence to operate, personnel representatives, the mayor of the local community, the director of the plant etc. etc.
- Who is then thinking of a systematic approach?
- First thing to find out is the cause. In fact, one wants the root cause.
- Mostly an accident is caused by a number of factors coming coincidentally together. Reproduction of the conditions may be rather difficult. Sometimes a cause never becomes clear because e.g. the evidence has been completely destroyed
- There are systematic methods developed to try to analyse and to distinguish main chain of events from side issues: e.g. ECFA

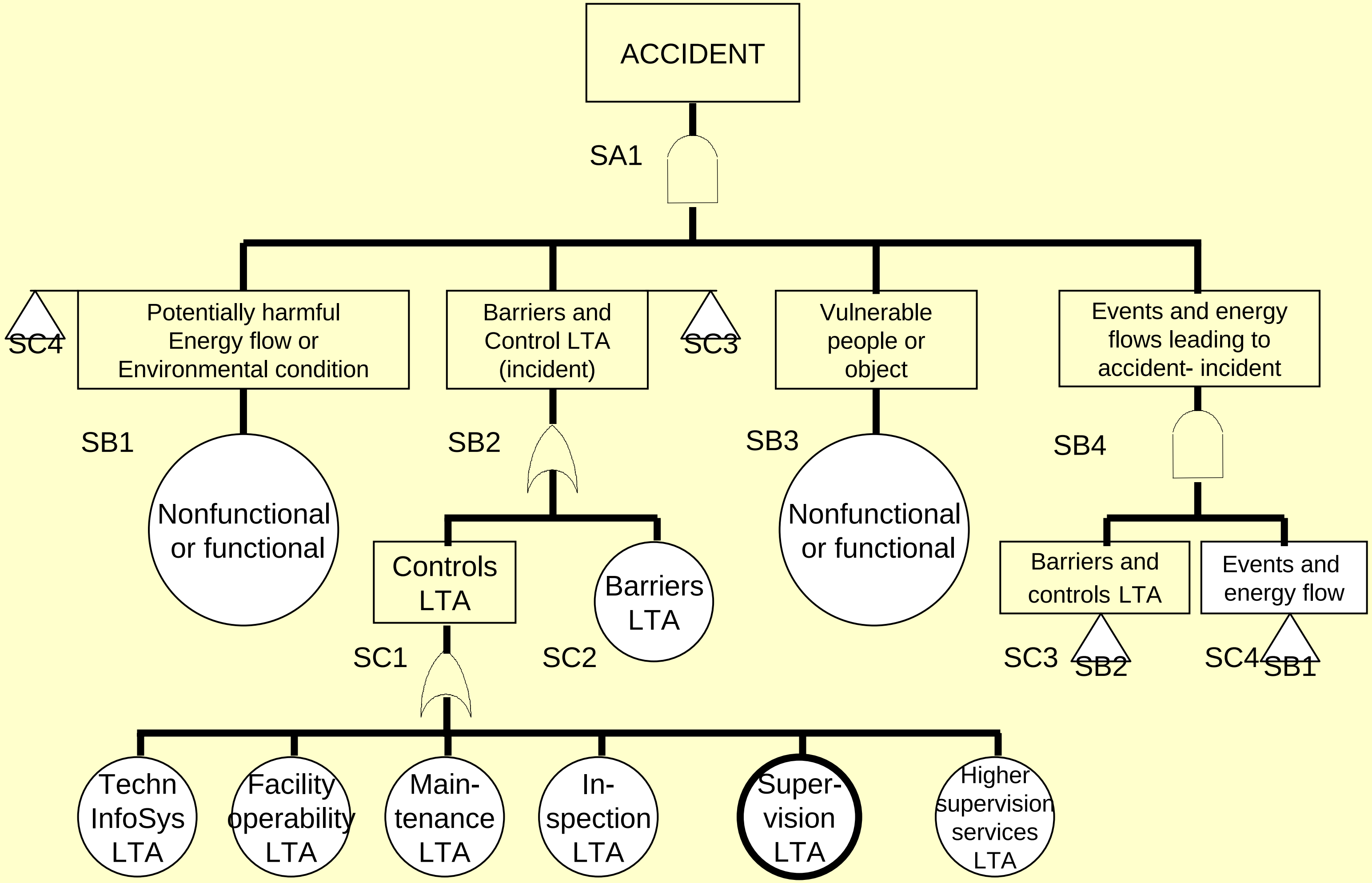
Source: Ferry, T.S., 1988, "Modern Accident Investigation and Analysis", 2nd Ed, John Wiley & Sons, Inc., USA, ISBN 0-471-62481-0

Events & Causal Factors Analysis



Accident investigation method : MORT

Management Oversight and Risk Tree: Events leading to accident



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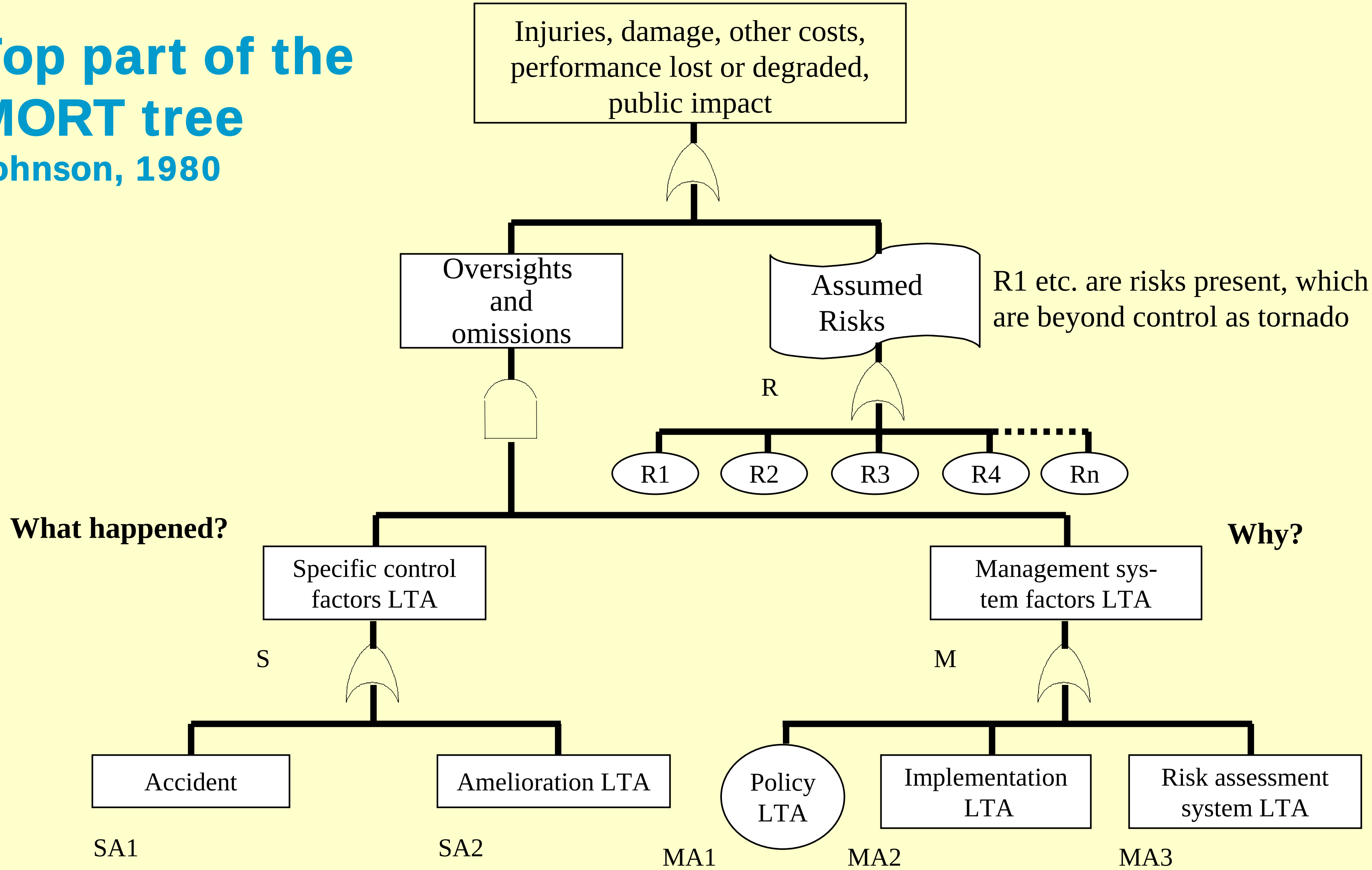
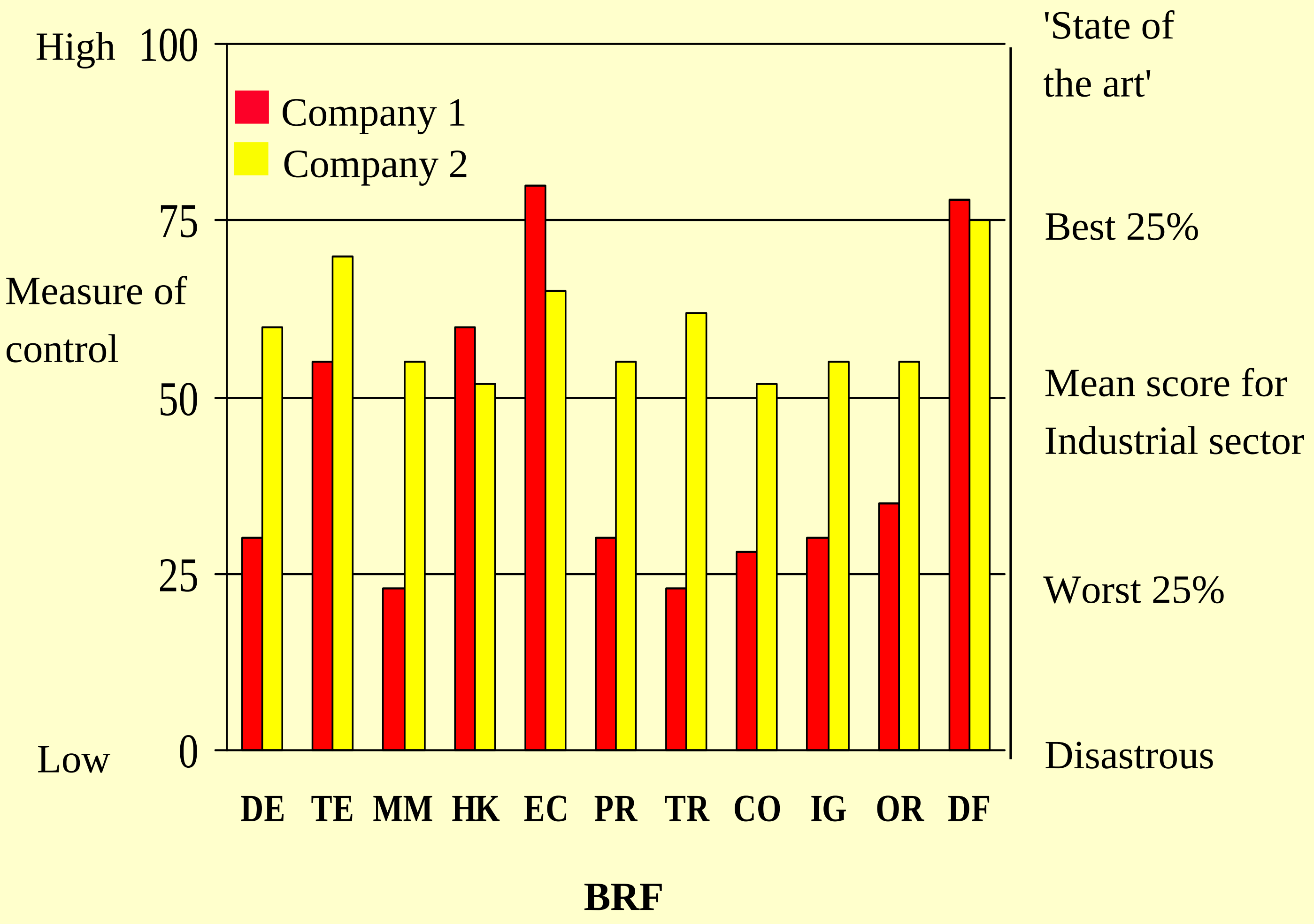
Top part of the MORT tree

Johnson, 1980



Tripod Condition Survey: Basic Risk Factors (Groeneweg)



Basic Risk Factors

Design (DE)

Tools & Equipment (TE)

Maintenance (MM)

Housekeeping (HK)

Error Enforcing Conditions (EC)

Procedures (PR)

Training (TR)

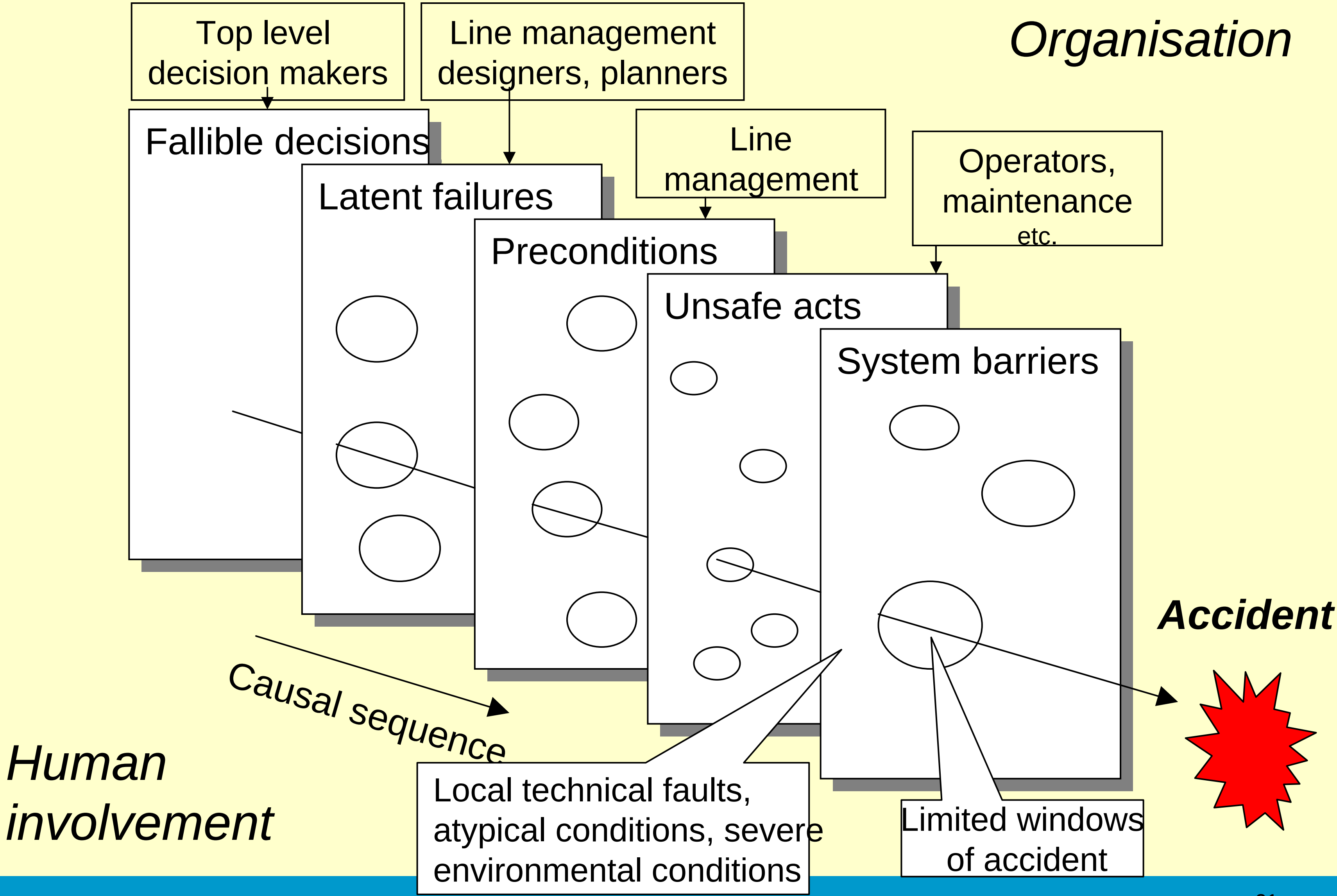
Communication (CO)

Incompatible Goals (IG)

Organisation (OR)

Defences (DF)

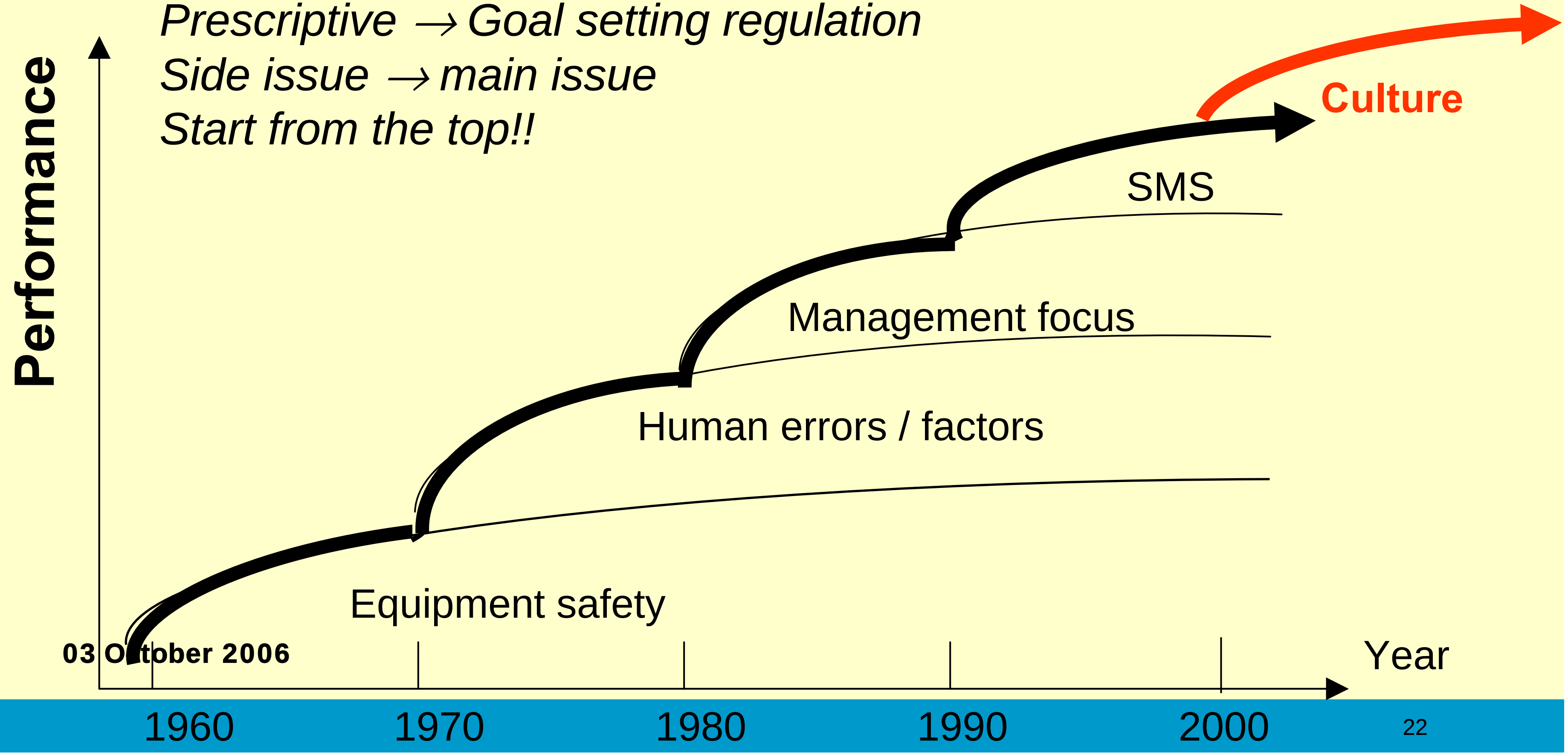
Shell's Tripod β : Accident causation sequence



Evolvement of safety management

Visser;source Proc. 8th Int´l Symp. Loss Prevention etc., Antwerp1995

From reacting upon accident → Prevention: Threat is plant closure
Safety officer only → All personnel involved
Prescriptive → Goal setting regulation
Side issue → main issue
Start from the top!!



Conclusions

1. **Hazard identification** requires experience. There is room for development of more efficient methods.
2. **Consequence analysis** is a lot of physics and engineering approaches. Many models are available but accuracy shall be largely improved to generate better confidence. This is especially true for the close-in effects.
3. **Failure rates** are a "pain in the neck" of the risk analyst. Let us try to get for hydrogen with its typical hydrogen embrittlement fractures and easy leakages reliable figures.
4. In **accident investigation** much human factor is involved. Concepts and models are available to do a systematic job. **Culture** is top!
5. Hydrogen production and filling plants will have their own set of generic **layers of protection**. These shall be studied in more detail.