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Original article

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MODELLING DISPERSION AND TOXICITY CONSEQUENCES DUE TO ACCIDENTAL RELEASE OF HYDROGEN SULPHIDE IN A CRUDE OIL REFINERY

Abstract: *Hydrogen sulphide (H2S) is a very toxic gas and is commonly encountered in crude oil refining processes. Atmospheric concentration as low as 300ppm could be fatal. Hence the need to periodically risk-assess H2S holding facilities in the light of inherent changes due to ageing equipment, wear and obsolescence, among others. This research studies the dispersion and toxicity consequences arising from the accidental release of H2S. The Fluid Catalytic Cracking Unit (FCCU) of Kaduna Refining and Petrochemical Company (KRPC) Ltd was used as a case study. Distances to six toxic concentration levels: 0.51, 15, 27, 50,100 and 300 ppm, and an average exposure time of 15 minutes were investigated. PHAST 8.2 software was used for the modelling and the inputs were obtained from actual plant design manuals, operations records and direct field measurements. The results indicate that H2S concentrations of 0.51ppm may be seen 183m downwind of the release point, 0.51ppm H2S and higher concentrations can present a significant risk to the public. Higher concentrations were observed at shorter distances downwind. In particular, 300 ppm H2S concentration was observed 5m away from the leak source.*

Keywords: hydrogen sulphide, dispersion, consequence modelling, toxicity, fatality.

INTRODUCTION

Loss of containment of hazardous materials from process vessels/pieces of equipment is a major source of concern in the petrochemical industry. Such leakages/ruptures often result in fire, explosion, toxicity and/or commercial losses. Flixborough disaster in 1974 and toxic gas release in Seveso (Italy) in 1978 are examples of accidents involving the release of toxic material [1]. The hazards that occur because of chemical substance leakage include acute exposure due to the atmospheric dispersion of toxic gases and fires from the ignition of flammable substances that have leaked. Leakages of toxic gases present danger, not only within the plant but also to communities in the surrounding area especially if the leak is on a large scale [2, 3].

The need for consequence modeling of process plant and hazardous storage facilities continues to become more prominent as a result of a global drift towards larger and more complex units that handle toxic, flammable and otherwise hazardous chemicals, operating under higher temperature and pressure conditions.

The magnitude of loss containment, dispersion and consequence are governed by several factors, including material storage condition/properties, characteristics of the leak source and ambient conditions [4, 5]. Meteorology has a strong influence on the outcome of a release, as well as on the spatial distribution of plant physical components. For instance, for adiabatic expansion of single gas through an orifice, the mass flow rate can be calculated from [6]:

$$Q_m = C_d A P_o \sqrt{\frac{2gM_{wt}}{ZRT_o} \cdot \frac{\gamma}{\gamma - 1}\left[\left(\frac{P_2}{P_o}\right)^{2/\gamma} - \left(\frac{P_2}{P_o}\right)^{(\gamma+1)/\gamma}\right]} \quad (1)$$

Where: P_o is the absolute upstream pressure (Pa or N/m^2); P_2 is the downstream pressure (absolute - in case the release is not to atmosphere) (Pa or N/m^2); M_{wt} is the molecular weight (kg /$mole$); T_o is the upstream temperature (K); R is the ideal gas constant ($J/(K.mol)$; γ is the ratio of the specific heats (dimensionless); g is the acceleration of gravity (m/s^2); C_d is the coefficient of discharge(dimensionless); Z is the compressibility factor (dimensionless), which is usually taken to be unity, assuming ideal gas behaviour.

The wind speed is affected by the earth's surface characteristics and increases with height above the ground according to a power function, suggesting that it is important to define a reference height always. A general equation for near-neutral and stable wind profile is given below [7]:

$$\frac{Uw}{U*} = \frac{1}{K} . (\frac{lnz}{z0} + 4.5\ \frac{z}{l}) \quad (2)$$

Where Uw is the wind speed, U* is friction velocity constant, which is assumed as equivalent to about 10%

of the wind speed at 10 m, k is von Karman's constant, z is the height, z_o is the surface roughness length parameter, and L is the Monin-Obukhov length.

Passive dispersion is governed by the atmospheric turbulence and is the final outcome of any gas and vapour release. As passive dispersion prevails, the importance of released fluid properties decreases, since its fate is predominantly determined by air convective motion by wind and by weather characteristics. A large and comprehensive literature has been developed, which provides accurate and detailed prediction data on the Gaussian behaviour of passive plumes [8]. Momentum-Jet to Passive-Plume Transition is the case of substances with molecular weight or apparent density which are comparable to air density, such as ethylene and hydrogen sulphide, buoyancy does not significantly affect the gas behaviour. For this point study, passive dispersion will be assumed as the governing dispersion mechanism.

The dispersion model used in PHAST is UDM (Unified Dispersion Model). It can model jet, dense, buoyant and passive dispersion. The toxic model calculates the toxic dose, the Probit number, the probability of death, the integrated probability of death and the exposure duration of an observer to finite concentrations of a dispersing cloud. Toxic load (L), Probit number (Pr) and the probability of death (Pdeath) and are given as follows [9]:

$$L = \int_0^T (C(x,t)^N dt \quad (3)$$

$$P\mathrm{T} = A + B\, ln(L) \quad (4)$$

$$P\mathrm{death} = 1/2\big(1 + erf((Pr - 5)/\sqrt{2}\big) \quad (5)$$

Consequence modeling refers to the calculation of numerical values (or graphical representation) that describes the credible physical outcomes of loss of containment scenarios involving f1ammable, explosive and toxic materials with respect to their impact on people, assets or safety functions. The consequence modeling in this study focuses on the dispersion and toxic consequences of Hydrogen sulphide release. Consequence models are typically nonlinear and multidimensional; hence they are solved using computers embedded in specialised software packages. PHAST is software that has been validated using experimental data by a number of individuals and organizations [10]. PHAST is a comprehensive line analysis tool for line analysis of the danger and determination of secure privacy.

The software allows the user to integrate and analyze nonlinear and multi-component systems [11]. Nadimi *et al.* [12] and Golubnichiy [13] used PHAST to model the dispersion of CO_2 and the pollution effects and identified distances to Lethal Concentration (LC) 50ppm and concentrations that are Immediately Dangerous to Life or Health (IDLH) for hydrogen sulphide as 224 meters and 386 m, respectively. Also, Jianwen and Wenxing, [14] employed PHAST to analyze gas transmission and distribution accidents. The results showed that societal risk varies significantly with different factors, including population density, distance from the pipeline, operating conditions and so on. Chiara *et al* [15] used PHAST to design a conceptual model for risk assessment of hazards due to CO_2. This work showed the results of risk analysis conducted in the proposed network for transporting CO_2 and the potential risks on the nearby population [16].

Case Study - process description

The Fluid Catalytic Cracking Unit (FCCU) of Kaduna Refining and Petrochemical Company (KRPC) Ltd was designed with a capacity of 133 m^3/hr using Kellogg Brown & Root (KBR) stacked design license [16]. The design is a 2-stage regeneration – partial combustion configuration yielding flue gas rich in Carbon Monoxide CO, which is further burnt in the CO Boiler to generate High Pressure (HP) Steam from High-Pressure Boiler Feed Water. Heavy gas oils, light vacuum gas oil and heavy vacuum gas oil are the feed streams to the fluid catalytic cracking unit. The FCCU breaks up the heavy oils into more volatile gasoline materials. The feed is introduced into the unit via the surge drum then it passes through a series of heat exchangers and passes to the fresh feed furnace to raise the temperature further to the required temperature of 320 ^oC. It is sent to the converter for conversion into light products. During its passage through the riser, most of the FCCU feed is broken down into light Olefins, FCC gasoline, a diesel range stream (light cycle oil), and a small amount of heavier oil (decanted oil) which can be blended into a bunker or other heavy fuel oil [16].

METHODOLOGY

The following data were collected from FCCU, KRPC: composition of materials flowing through equipment and pipeline, the flow rate of materials passing through pipelines and equipment/pipeline conditions (phase, temperature, pressure) then a hazard identification, formulation of credible scenario and finally the consequence modelling step, these are shown in Figure 1.

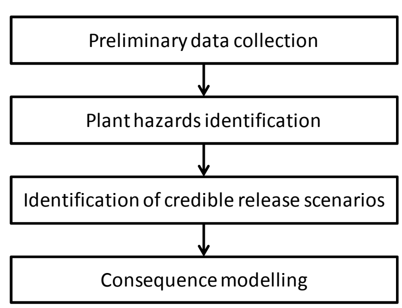

Figure 1: The methodology outline

To formulate a structured approach to the identification of hazards it is essential to understand contributory factors. These factors include inventory analysis which was used in understanding the relative hazards and shortlisting of release scenarios. Once the events are initiated, both the complexity of the study and the number of incident outcome cases become affected by the range of initiating events and incidents. In this study, a scenario featuring a catastrophic rupture of a vessel was chosen. Parameters, such as potential vapour release, depend significantly on the operating conditions. This operating range is was chosen to be very representative, as detailed in the following sections (Table 1-3)

Modelling Assumptions

The study considers the dynamics of H2S in a mixture, not as a single isolated component. It was also assumed that the mixture composition does not change during the different stages of the discharge and dispersion. The properties of the mixture were be calculated from the component properties using simple averaging and equations of state (Soave-Redlich Kwong and Peng-Robinson). A flashing correlation and conservation of momentum were assumed for the toxic dispersion of H_2S [17, 18]. In PHAST, events are modelled based on the process conditions, atmospheric conditions and release point properties. Real plant design and operations data were used as inputs for the modelling. Some of the parameters, such as weather conditions, wind direction and release elevation are inherently difficult to define with exactitude; as such, typical values were used.

Table 1: Input Parameters to PHAST

Leakage Parameter	Value		Weather Parameter	Value
Hole (Orifice diameter)	10 mm		Wind speed [m/s]	3.6
Release location (Elevation)	3 m		Pasquill stability	B , A/B
Concentration of interest (ppm)	0.51,15,27, 50,100 & 300		Atmospheric temperature [ºC]	28
Averaging time for the concentration of interest	ERPG,IDLH,STEL		Relative humidity [fraction]	0.25
Averaging time for reports (ERPG [1 hr])	Yes		Solar radiation flux [kW/m2]	0.5
IDLH [30 mins]	Yes		Wind speed at height [m/s]	4.3365
STEL [15 mins]	Yes			
Number of toxic levels	4			

Study Scenario

This study seeks to study the dispersion behaviour of H_2S, leaking from the Reactor-Regenerator within the Fluid Catalytic Cracking Unit (FCCU) of KRPC. Areas affected by H_2S concentrations ≥ 0.51ppm around FCCU were identified. Specifically, six H_2S exposure concentrations (0.51, 15, 27, 50,100, and 700 ppm), under a single atmospheric condition and varying average exposure time in line with the ERPG, IDLH and STEL thresholds, were considered. A number of hole sizes and atmospheric conditions were assessed to gauge the sensitivity of the results to them, further details are presented in Tables 1 -3. The stream composition, operating conditions and design conditions of the unit were collected from the process manual to identify the release variables for a 7043kg/hr (1.96kg/s) mass inventory.

Table 2: Fuel Gas Stream composition

Component	% mole
Carbon dioxide	1.1
Hydrogen	12.8
Methane	38.92
Ethylene	18.34
Ethane	11.23
Hydrogen sulfide	2.33
Propylene	3.49
Propane	1.07
N-Butane	2.42

Table 3: Typical KRPC Weather Data

Wind speed [m/s]	3.6
Pasquill stability	B unstable - as with A/B only less sunny or windier
Atmospheric temperature [degC]	28
Relative humidity [fraction]	0.25
Solar radiation flux [kW/m2]	0.5
Wind speed at height [m/s]	4.3365

This study applied the exposure index of H_2S toxicity using three-level criteria: Emergency Response Planning Guidelines (ERPG), Short Term Exposure Limits (STEL) and Immediately Dangerous to Life or Health (IDLH) to determine hazard contours.

RESULTS AND DISCUSSION

The results are presented in tables, maps and graphs. The dispersion charts are shown in Figure 2(a –f). The actual distances and the corresponding concentrations are summarized in Table 5.

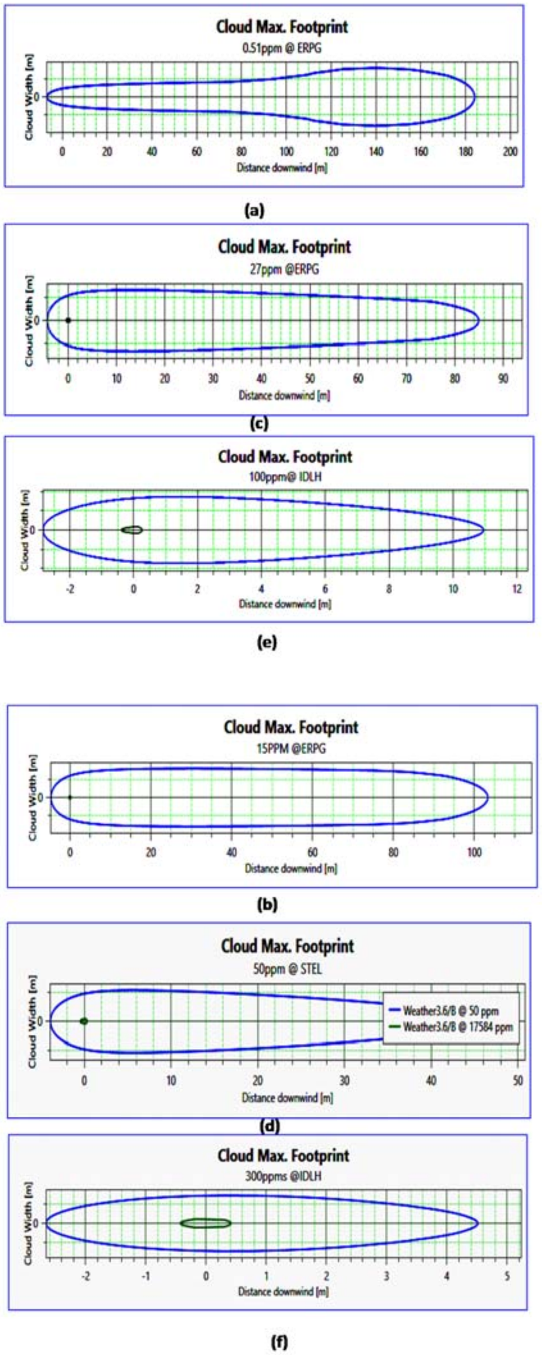

Figure 2: Graph of the cloud maximum footprint against the distance downwind

Expectedly, higher concentrations were observed at shorter distances downwind. For instance, 15ppm was seen at about 103 m, 27ppm at 85 m, 50ppm at 46 m, 100ppm at 18 m and 300ppm within 5 m radius. The maximum cloud footprint was also superimposed on the refinery map to assess toxicity effects at specific locations within the plant. Sample Cloud mapping for 0.51ppm and 300ppm were shown in Figure 3.

Table 5: Distance downwind to defined concentrations

Scenario	The concentration of interest [ppm]	Averaging time selected	Distance downwind to the concentration of interest [m]
0.51ppm @ ERPG	0.51	ERPG	183.434
15 ppm @ERPG	15	ERPG	103.237
27 ppm @ERPG	27	ERPG	84.891
50 ppm @ STEL	50	STEL	45.666
100 ppm @ IDLH	100	IDLH	17.802
300ppms @IDLH	300	IDLH	4.498

Figure 3(a): Cloud radius (183 m) for 0.51 ppm H_2S-superimposed on the plant map

Figure 3(b): Cloud radius (5m) for 300 ppm H_2S-superimposed on the plant map

Concentration quantification and GIS mappings against distances are important metrics for risk assessment and mitigation purposes. They provide indicative insights into the toxic effects on receptors of interest (within a radius of coverage). For instance, to choose appropriate toxic gas detector model, installation height, location and orientation, the cloud footprints will be necessary to quantitatively optimise the space coverage – boosting detection probability while cutting down on the number of detectors to be purchased.

CONCLUSION

The Fluid Catalytic Cracking Unit (FCCU) of Kaduna Refining & Petrochemical Company (KRPC) Ltd presents significant toxicity hazards. Specifically, based on the mild assumptions made, Hydrogen Sulphide (H_2S) concentrations in the range of 0 – 27ppm could be observed within a 200m radius of the leak source in the FCCU. Concentrations in the range of 50 - 300 ppm may be seen within a 50m radius. These metrics provide important prioritization bases for toxicity risk management. In particular, the detector spatial installation exercise could be guided by these results. For instance, the inner zone (50m radius) may need higher integrity and more detectors and alarm systems. The identified downwind direction and plume heights will also provide clues on areas of priority. So, the results could be used to maximise H_2S leak detection while cutting down on the number of detectors to be purchased. The result would also help KRPC management in planning and preparing against emergencies involving H_2S leaks within the FCCU.

NOMENCLATURE

P_o	*absolute upstream pressure*
API	*American Petroleum Institute*
C_d	*Coefficient of discharge*
ERPG	*Emergency Response Planning Guidelines*
FCCU	*Fluid Catalytic Cracking Unit*
GRAD	*Gas Release And Dispersion*
HP	*High Pressure*
IDLH	*Immediately Dangerous to Life or Health*
k	*Von Karman's constant*
KBR	*Kellogg Brown & Root*
KRPC	*Kaduna Refining and Petrochemical Company*
L	*Toxic load*
LD	*Lethal Concentration*
M_{wt}	*Molecular weight*
P_2	*Downstream pressure*
Pdeath	*Probability of death*
PHAST	*Process Hazard Analysis Software Tool*
ppm	*Parts per million*
Pr	*Probit number*
STEL	*Short Term Exposure Limit*
*U**	*Friction velocity constant*
UDM	*Unified Dispersion Model*
Uw	*Wind speed*
y	*Specific heats ration*
z	*Height*
Z	*Compressibility factor*
zoi	*Surface roughness length parameter*

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MODELIRANJE POSLEDICA DISPERZIJE I TOKSIČNOSTI USLED SLUČAJNOG ISPUŠTANJA VODONIK-SULFIDA U RAFINERIJI NAFTE

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Rezime: Vodonik sulfid (H_2S) je veoma toksičan gas koji se obično javlja u tehnološkim procesima obrade sirove nafte. Ovaj gas može biti smrtonosan čak i ako je prisutan u veoma malim količinama u vazduhu, na primer 300 ppm. Iz toga proizilazi potreba za periodičnom procenom rizika u objektima u kojima se skladišti H_2S, između ostalog zbog dotrajalosti opreme i habanja. U radu je predstavljena analiza posledica disperzije i toksičnosti ovog gasa usled slučajnog ispuštanja. Za studiju slučaja uzeta je Rafinerija nafte i petrohemijskih proizvoda u Kaduni (Nigerija), Odeljenje za katalitičko krekiranje fluida. Ispitivano je rastojanje u šest nivoa koncentracije toksičnosti: 0,51, 15, 27, 50,100 i 300 ppm; i prosečno vreme izlaganja u trajanju od 15 minuta. Za modeliranje je korišćen softver PHAST 8.2, a početne vrednosti su dobijene iz uputstava za projektovanje postrojenja, evidencije o radu postrojenja i direktnih merenja na terenu. Rezultati pokazuju da se koncentracija H_2S od 0,51ppm mogu naći 183m nizvodno od tačke oslobađanja, dok koncentracije vodonik sulfida veće od 0,51ppm H_2S predstavljaju veoma visok rizik. Veće koncentracije primećene su na kraćim rastojanjima niz vetar. Konkretno, koncentracija H_2S od 300 ppm zabeležena je na 5m od izvora ispuštanja.

Ključne reči: vodonik-sulfid, disperzija, modeliranje posledica, toksičnost, smrtni ishod.