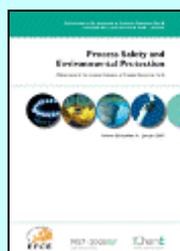


# Process Safety and Environmental Protection

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**Samith Rathnayaka, Faisal Khan, PaulAmyotte. *SHIPP methodology: Predictive accident modeling approach : part II. : validation with case study. Pages 75-88.***

System Hazard Identification, Prediction and Prevention (SHIPP) is a systematic methodology to identify, evaluate, and model the accident process, thereby predicting and preventing future accidents in a process facility. In this methodology, process hazard accidents are modeled using safety barriers rather than causal factors. The fault tree and event tree analysis techniques enhance the accident model to represent a holistic picture of the cause-consequence mechanism of the accident process. Quantitative analysis has two aspects: updating and prediction. The Bayesian theory updates failure probability and consequence occurrence probability when a new observation arrives. The predictive model forecasts the probability of a number of abnormal events occurring in the next time interval. The qualitative and quantitative capabilities of the SHIPP methodology help to design and implement safety strategies into a process system. This methodology was presented in Part I of a series of two papers. This paper (Part II) presents the results of a case study carried out on a liquefied natural gas (LNG) facility. It is conducted with the sole purpose of testing the SHIPP methodology. Gas production and liquefaction were considered as a boundary for accident analysis. This paper illustrates accident model development and cause-consequence analysis for the LNG facility. The updated results demonstrate that the probabilities of abnormal events dramatically change over time as new information is observed. Using accident precursor data for the year 2009, the predictive model estimates that the mean of abnormal events occurring in the next time interval is 22. The qualitative and quantitative analyses provide insight to identify critical safety areas and functions, and to determine the likelihood of failure of these measures. Combining management oversight and engineering analyses, the SHIPP methodology provides a comprehensive, systematic approach to manage a system risk. **Research highlights:** ►The SHIPP methodology provides an easy and effective mechanism to model process accident and integrates its results in process safety management system. ►Process accident model is developed with predictive capabilities using safety barriers concepts. ►The developed model is able to capture the occurrence behavior of an accident and update the accident likelihood using the Bayesian updating mechanism. ►The predictive model help to forecast the number of abnormal events in the next time interval given operation characteristics of the process system and accident precursor information. ►Application of the proposed methodology and developed accident model is demonstrated on a gas processing facility using real life plan data.

- **Keywords:** System hazard identification; Prediction and prevention (SHIPP) methodology; Process hazards; Safety barrier; BAYESIAN updating; Predictive model

**Jian-wei Cheng, Sheng-qiang Yang. *Improved Coward explosive triangle for determining explosibility of mixture gas. Pages 89-94.***

It is very important to determine the explosibility of the mixture gas in the coal mine sealed area after a gas explosion occurred. If the combustible mixture gas has high explosive tendency, the potential re-occurring explosion would cause rescue workers' death when they proceed with their rescue operations in the accident mine. Therefore, no one is allowed to go down to the underground until the mixture gas is not explosive. Lots of methods have been developed to determine the explosibility of the mixture gas in the sealed area for a long time. One of these methods is the Coward explosive triangle method which was published by Coward in 1952. Because of its easiness and high efficiency to determine the explosibility of the mixture gas, it gradually becomes a very popular tool for mining engineers and rescue team members in the mining industry. However, although the Coward explosive triangle method has extensive applications, there are still a few drawbacks in this model. Consequently, errors may be introduced when applying. In this paper, a brief introduction of the Coward explosive triangle is described firstly. Then based on analyzing its drawbacks, some improvements with different aspects to calibrate the Coward explosive triangle are proposed and discussed. Finally, case demonstrations and comparisons with the old model are also shown. The results indicate that the improved Coward explosive triangles have better accuracy and reliability and could make more accurate judgments. **Research highlights:** ►The shape of the Coward explosive triangle is redefined. ►The position of the mixture gas point is corrected. ►The early warning index is proposed to track the movement of the mixture point. ►Case demonstrations indicate that the improved triangle has better accuracy.

- **Keywords:** Coward explosive triangle; Gas explosion; Explosibility of the mixture gas

**Basheer Hasan Diya'uddeen, Wan Mohd Ashri Wan Daud, A.R. Abdul Aziz. *Treatment technologies for petroleum refinery effluents : a review. Pages 95-105.***

This paper presents a brief account of different technologies used for the treatment of petroleum refinery effluents (PRE). Broadly, PRE treatment is accomplished in two stages, namely, a series of pre-treatment steps, in which suspended matter, oil and grease are reduced, and an advanced stage, in which wastewater contaminants are decreased to certain acceptable discharge limits. Photocatalytic degradation techniques have been widely used in water and wastewater treatment. However, the literature regarding PRE treatment is scarce, and the technique is still not being utilised on an industrial scale in refineries. This is largely due to limited research findings discussing PRE treatments. Most researches are focused on treating singular contaminants found in PRE, e.g., phenols, sulphides, oil, grease and other organic components. This review focused on works that investigated PRE treatment by monitoring general refinery wastewater parameters, namely, chemical oxygen demand (COD), biological oxygen demand (BOD), total petroleum hydrocarbon (TPH), oil and grease (O&G), sulphate and phenols at the advanced treatment steps. This paper presents an overview of photocatalytic degradation and discusses published works with the goal of presenting the technique as an attractive and viable process unit. If optimised, this process has great potential for replacing other separation and degradation treatment approaches employed at the advanced treatment stage for PRE. **Research highlights:** ►We are reporting current treatment processes for petroleum refining effluents (PRE). ►Biological methods and its various modified forms are the most widely used. ►Photocatalytic degradation

(PCD) is an attractive technique for the treatment of PRE. ►Petroleum refining industry is yet to embrace application of PCD to PRE due to scarce literature.

- **Keywords:** Photocatalytic degradation; Petroleum effluent; Environmental pollution

**Raymond R. Tan, Kathleen B. Aviso, Jose B. Cruz Jr., Alvin B. Culaba. A note on an extended fuzzy bi-level optimization approach for water exchange in eco-industrial parks with hub topology. Pages 106-111.**

In our previous paper, a fuzzy bi-level programming model was developed to determine optimal interplant water integration networks in eco-industrial parks (EIPs). This approach allowed the appropriate incentive mechanisms, in the form of fresh water and effluent fees as well as water reuse subsidies, to be optimized from the perspective of the EIP authority. This work extends the original mathematical model by modifying the role of the EIP authority to include water regeneration and redistribution via a centralized hub. The resulting fuzzy bi-level programming model may then be solved to yield a "satisficing" solution that reflects a reasonable compromise between the EIP authority's desire to minimize fresh water usage, and the participating companies' desire to minimize costs. A case study is used to illustrate the modeling approach. **Research highlights:** ►A novel bi-level optimization model for designing water exchange networks in eco-industrial parks (EIPs) was developed. ►The model focuses on EIPs with hub topology where stream exchanges among companies are done through a centralized facility. ►The bi-level optimization approach accounts for the interactions between the EIP authority and the participating companies using a Stackelberg game framework.

- **Keywords:** Eco-industrial park; Interplant water network; Stackelberg game; Bi-level programming

**Yanyu Wu, Shaoqi Zhou, Xiuya Ye, Dongyu Chen, Ke Zheng, Fanghui Qin. Transformation of pollutants in landfill leachate treated by a combined sequence batch reactor, coagulation, Fenton oxidation and biological aerated filter technology. Pages 112-120.**

A combination process was developed including sequence batch reactor (SBR), coagulation, Fenton oxidation, and biological aerated filtering (BAF) in series for the purpose of removing pollutants in landfill leachate. The high contents of dissolved organic matters (DOM) of landfill leachate in each treatment process were fractionated into humic acid (HA), fulvic acid (FA), and hydrophilic (HyI) fractions. The composition changes and characteristics of DOM were investigated. Subsequently, seventy organic micropollutants in raw leachate were detected, and twenty-five organic pollutants were completely removed by SBR process. Low organic pollutants and high turbidity removals were achieved by coagulation. Thirty-seven organic micropollutants disappeared completely in Fenton effluent and low molecular weight fractions were removed by BAF preferentially. A total reduction of COD (98.4%), BOD<sub>5</sub> (99.1%), NH<sub>4</sub>-N (99.3%), TP (99.3%), SS (91.8%), turbidity (99.2%) and color (99.6%) achieved in the final BAF effluent indicated the effectiveness of the combined plant. Moreover, metal ions of Cu, Ni, Zn, Mn, Cr, Mg, Pb, Cd, Al, Fe and anions of SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup> in raw leachate and four treated effluents were measured, respectively. The observations indicated that leachate treated by the combined process still contained higher concentration of total heavy metals and inorganic anions than the surrounding water environment, though no violation to effluent standard was found. The possible risk in leachate should not be negligible because landfill leachate was still one of the major sources of heavy metals and inorganic pollutants discharged to the surrounding environment. **Research highlights:** ►The fates of various pollutants in a combined landfill leachate treatment were investigated. ►The level of organic pollutants in

combined effluent met standard for wastewater discharge. ►The concentration of total heavy metals should not be negligible in combined treatment effluent.

- **Keywords:** Landfill leachate; Combined treatment process; Humic substances; Micropollutant; Heavy metal

**Shengli Niu, Kuihua Han, Chunmei Lu. *An experimental study on the effect of operating parameters and sodium additive on the NO<sub>x</sub>OUT Process.* Pages 121-126.**

An experimental study on the nitric oxide (NO) reduction through the NO<sub>x</sub>OUT Process has been conducted on a drop tube furnace experimental system. At 1223 K, when stoichiometric ratio of urea to NO ( $\beta$ ) is fixed at 1.5 and 2, the maximum NO reduction efficiency of 70.19% and 78.89% could be achieved, respectively. The efficiency curve is presented as a reversed "V" as a function of temperature and the corresponding "temperature window" is 108 K and 154 K at  $\beta = 1.5$  and 2. Also, these two  $\beta$  values are preferable to determine injected urea quantity. As oxygen concentration is increased from 1.5% to 4.5%, efficiency is continuously depressed from 68.35% to 55.37% at  $\beta = 1.5$  and from 77.87% to 62.76% at  $\beta = 2$ . At the same time, residence time ( $\tau$ ) should be guaranteed at least 0.61 s for thorough NO reduction. When 50 ppm of NaOH, 25 ppm of Na<sub>2</sub>CO<sub>3</sub> or 50 ppm of CH<sub>3</sub>COONa is injected as promoted additive, the maximum NO reduction efficiency is, respectively, heightened to 82.07%, 81.36% and 81.81% at  $\beta = 1.5$  and these values are even higher than the ones which are achieved at  $\beta = 2$  if no additive is injected. For both  $\beta = 1.5$  and 2, efficiency improvement becomes slow when NaOH is increased to 20 ppm. Meanwhile, when NaOH is injected at  $\beta = 2$ , efficiency of above 90% could be achieved and this value is comparable to the one achieved in advanced reburning. **Research highlights:** ►Characteristic of NO reduction during the NO<sub>x</sub>OUT Process is investigated on a drop tube furnace experimental system. Influencing factors of the reaction temperature, the normalized stoichiometric ratio of nitrogen reducing agent to NO ( $\beta$ ,  $\beta = 2 \times$  molar ratio of NH<sub>2</sub>CONH<sub>2</sub>/NO for urea), the oxygen concentration (O<sub>2</sub>) and the residence time ( $\tau$ ) are investigated. ►The maximum NO reduction efficiency of 70.19% and 78.89% could be achieved at 1223 K when  $\beta$  is set at 1.5 and 2, respectively. The corresponding "temperature window" is 108 K and 154 K. Efficiency is continuously depressed from 68.35% to 55.37% at  $\beta = 1.5$  and 77.87% to 62.76% at  $\beta = 2$ , when O<sub>2</sub> is increased from 1.5% to 4.5%.  $\tau$  should be guaranteed at least 0.61 s. ►Sodium hydroxide (NaOH), sodium carbonate (NaCO<sub>3</sub>) and sodium acetate (CH<sub>3</sub>COONa) are selected as the additives. Their promoted effect on the NO<sub>x</sub>OUT Process is emphasized. ►When 50 ppm of NaOH, 25 ppm of Na<sub>2</sub>CO<sub>3</sub> or 50 ppm of CH<sub>3</sub>COONa is injected, the maximum efficiency is heightened to 82.07%, 81.36% and 81.81% at  $\beta = 1.5$ . These values are higher than the ones under the  $\beta = 2$  condition without additive injection. For both  $\beta = 1.5$  and 2, improvement of efficiency becomes slow when NaOH is increased to 20 ppm. When NaOH is injected at  $\beta = 2$ , efficiency of above 90% could be gained. This is comparable to the one achieved in advanced reburning.

- **Keywords:** Urea; Selective non-catalytic reduction (SNCR); Nitric oxide (NO); Additive

**Wensheng Wang. *Chelating adsorption properties of Cd(II) on the PMAA/SiO<sub>2</sub>.* Pages 127-132.**

In this paper, functional macromolecule poly (methacrylic acid) (PMAA) was grafted onto the surface of silica gel particles using 3-methacryloxypropyl trimethoxysilane (MPS) as intermedia, and the grafted particle PMAA/SiO<sub>2</sub> with strong adsorption ability for Cd<sup>2+</sup> was prepared. The adsorption properties of Cd<sup>2+</sup> on the PMAA/SiO<sub>2</sub> were investigated with both batch and column methods. The experimental results showed that the PMAA/SiO<sub>2</sub> possesses very strong adsorption ability for Cd<sup>2+</sup>, and the saturated

adsorption amount could reach up to  $42.6 \text{ mg g}^{-1}$ . The equilibrium adsorption data were found to be consistent with the Langmuir isotherm model. pH and temperature have great influence on the adsorption amount. PMAA/SiO<sub>2</sub> can be easily regenerated using diluted hydrochloric acid solution as eluent. The PMAA/SiO<sub>2</sub> possesses excellent reusability properties as well. **Research highlights:** ▶The PMAA/SiO<sub>2</sub> possesses very strong adsorption ability for Cd<sup>2+</sup>. ▶The PMAA/SiO<sub>2</sub> possesses very strong adsorption ability for Cd<sup>2+</sup>. ▶The equilibrium adsorption data are consistent with the Langmuir isotherm model. ▶PMAA/SiO<sub>2</sub> can be easily regenerated.

- **Keywords:** Chelating adsorption; Cadmium ion; Poly (methacrylic acid); Silica gel

**Wen-Juan Hu, Cheng-Gang Niu, Ying Wang, Guang-Ming Zeng, Zhen Wu. Nitrogenous heterocyclic compounds degradation in the microbial fuel cells. Pages 133-140.**

Growing energy needs and concerns about environmental pollution have stimulated increased interest in the research and application of microbial fuel cell (MFC) systems. The objective of this study was to investigate possible electricity production with nitrogenous heterocyclic (N-heterocyclic) compounds degradation in the MFCs. Two-chamber MFCs were designed and inoculated with anaerobic sludge acclimated for several months. The experiments were conducted to test the potential for biodegradation of refractory organic matters and electricity generation using representative N-heterocyclic compounds such as pyridine, quinoline and indole. A maximum voltage of 524 mV, 494 mV, 413 mV (based on an external resistance of 1000 Ω), and the corresponding maximum power densities of  $228.8 \text{ mW m}^{-2}$ ,  $203.4 \text{ mW m}^{-2}$ ,  $142.1 \text{ mW m}^{-2}$  were obtained from pyridine, quinoline, and indole, respectively. Meanwhile, the maximum degradation efficiency of these substrates and COD (chemical oxygen demand) removal were up to 90% and 88%, respectively. The metabolic intermediate products were detected by GC/MS analyses of the anode solution. These results indicated that N-heterocyclic compound may be used as the MFC fuel in practical applications of wastewater treatment. **Research highlights:** ▶ The microbes from anaerobic sludge were various and easy to obtain. ▶ The toxic and refractory N-heterocyclic compounds were used as carbon sources, which indicated MFC technology could be linked with wastewater treatment in practical applications. ▶ The metabolic pathways of N-heterocyclic compound under anaerobic conditions were investigated by GC/MS, which provide some new information for biological treatment of these target compounds (pyridine, quinoline, indole).

- **Keywords:** Nitrogenous heterocyclic compounds; Degradation; Microbial fuel cell; Electricity generation

**S.P. Sivapirakasam, Jose Mathew, M. Surianarayanan. Constituent analysis of aerosol generated from die sinking electrical discharge machining process. Pages 141-150.**

This paper aims to study the influence of process parameters on the breathing zone concentration of the aerosol generated from the electrical discharge machining process using Taguchi methodology. Peak current, pulse duration, dielectric level above the spark location and flushing pressure were the process parameters considered in this work. Characterization of the components present in the aerosol and its morphology are also presented. The metallic particles present in the aerosol were analyzed using Inductively Coupled Plasma (ICP). Gas Chromatography coupled with Mass Spectrometry (GC-MS) was used to analyze the hydrocarbon components attached to the aerosol. Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) techniques were applied to study the morphology of aerosol. Analysis of the results showed that the peak current and the pulse duration are the most significant parameters on the breathing zone concentration of aerosol. Investigation using ICP revealed that the major portion of aerosol (about

69%) constitutes metallic particulates. GC-MS analysis of the aerosol samples indicated the presence of about 20 different hydrocarbons. Morphology studies showed that the particulates are of spherical shape with average sizes ranging from 20 to 29 nm. The control measures to minimize the risk of exposure have also been discussed in this paper. **Research highlights:** ▶ Emission of aerosol is an important occupational threat of die sinking EDM process. ▶ Peak current and the pulse duration are the most influential parameters in the generation of aerosol. ▶ 69% of aerosol generated from the EDM process constitutes of metallic particles. ▶ Aerosol emissions from the EDM process are attached with a complex mixture of about 20 hydrocarbons. ▶ The particle size of the aerosol was observed in the range of 25–29 nm.

- **Keywords:** Electrical discharge machining; Aerosol; Taguchi methods; Occupational exposure; Nanosized particles