**Химия. Текст 1.**

**Analysis of Different Pressure Thermally Coupled Extractive Distillation Column**

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**Abstract:** In this contribution, a different pressure thermally coupled extractive distillation process has been applied on the separation of propylene and propane with aqueous acetonitrile (ACN) solution as entrainer. The novel distillation process integration is the combination of different pressure thermally coupled distillation (DPTCD) and extractive distillation (ED). Both the new process and the conventional process have been simulated in Aspen Plus. Sensitivity analysis has been conducted to select an appropriate compression ratio and other operating parameters based on the priority that the propylene product purity is 99.2 wt % and less energy consumption. The influence of the proposed distillation column on energetic and economic aspects is evaluated through intensive comparison against the conventional stand-alone column, and better performance is achieved with up to 46.02% energy saving and close to 9.7% saving in total annual cost (TAC).

**Keywords:** Different pressure thermally coupled, Extractive distillation, Propylene, Propane, Energy saving, TAC.

**1. INTRODUCTION**

Distillation is a unit operation most widely used in petro-chemical processes [1], which is also known for its high energy requirement and poor thermodynamic efficiency. Propylene is mostly used to produce polypropylene, acrylonitrile, propylene oxide and acetone. With the increasing of demand for propylene derivatives, the production of propylene has become more and more important. Since most propylene comes from pyrolysis gases, the separation of propyl-ene in ethylene projects behaves great commercial significance. In ethylene projects, propylene is purified from a mixture mainly composed of propylene and propane [2].

Because the boiling points of propane and propylene are very close over a large range of pressure, it always needs a huge investment in equipment and much energy requirement to separate them by conventional distillation. Extractive distillation (ED), an important separation method in chemical engineering [3, 4], is used to separate compounds with similar boiling points by using an additional entrainer to alter the relative volatility [5]. Liao *et al*. [2] had used extractive distillation for the propane–propylene separation and achieved excellent purity of propylene. The ED makes separation easy, but it still needs considerable energy requirement be-cause of the addition of entrainer.

Distillation requires a large proportion of the energy used in the chemical process industries. Consequently, there is a significant incentive to improve the energy efficiency [6] of this widely applied separation process [7]. Li *et al*. [8] pro-posed the general structure of different pressure thermally coupled distillation (DPTCD) column. For a typical DPTCD column, the conventional distillation column is divided into two columns with different pressures, a high–pressure (HP) column and a low–pressure (LP) column. The overhead vapor of the HP column is used as the heat source of the reboiler of the LP column, therefore the thermally coupled process is realized and this intensified energy integration approach reduces the steam consumption in the reboiler and avoids the use of a condenser. The DPTCD technology is used in the separation of propane–propylene and C4’s hydrocarbon, and comparing with conventional distillation, the energy requirement could be reduced by 92.3% and 87.1%, respectively.

**Химия. Текст 2.**

**Investigation of Particulate Flow in a Channel by Application of CFD, DEM and LDA/PDA**

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**Abstract:** Hydroabrasion in particulate flows plays an important role in various industrial and natural processes. To predict the influence of it in a pipeline, channel or a fitting, it is essential to characterize the effects in a simple standardized geometry. An example to this is a pipe channel with a cylindrical obstacle adjusted inside the channel perpendicular to the flow direction. Results of flow field are generated by using the non-invasive Laser/Phase Doppler Anemometry (LDA/PDA) measurement technique. The velocity profiles of single phase and particulate flow from computational fluid dynamics (CFD) and discrete element method (DEM) simulations were validated by the LDA experimental data. The simulations were performed on the basis of Euler-Lagrange technique for both CFD and DEM. The measurements show that a Karman vortex field forms behind the obstacle and particles move inside this field with an average negative velocity of up to 25% of the fully developed velocity field. A comparison of CFD and DEM results with experimental data showed that in Karman velocity field, the CFD results fit better to the LDA measurements. In the fully developed flow region and also above and under the vortex field behind the obstacle, the DEM results match better with the LDA data.

**Keywords:** CFD, cylindrical channel, DEM, hydroabrasion, LDA/PDA.

**1. INTRODUCTION**

Particulate flows are responsible for accelerated abrasion

in pipelines and plant equipment which significantly shortens

the service life and increase the repair and maintenance

costs and is an important factor which should be considered

in a sustainable design. The existing literature mainly covers

LDA and Particle Image Velocimetry (PIV) measurements

of gas-liquid multiphase flow systems with very few references

on solid particles-liquid flows. To our best knowledge,

data on velocity profiles of solid particles and the deviation

compared to the liquid phase, velocity fluctuations and the

particles size distribution has not been measured with

LDA/PDA technique for solid particles-liquid flows with

sufficient detail and accuracy.

Sommerfeld [1] reviewed a series of experimental works

concerning the achievement of a detailed analysis of solid

particles entrained in a gas flow in pipes and channels.

Huber and Sommerfeld [2] applied the PDA and a laser light

sheet technique to measure the solid particles concentration

in a pipe along the cross section. Moreover, a very detailed

set of experiments was provided by Tsuji and Morikawa [3]

for a gas–solid flow in a horizontal pipe using various types

of relatively large spherical particles. Ozgoren *et al.* [4] applied

PIV to investigate and compare the flow structures in

the downstream region of a cylindrical and spherical obstacle

fixed in a channel flow. Kumara *et al.* [5] has compared the

PIV and LDA measurement techniques applied to the oilwater

two phase flow in a horizontal pipe.

**Химия. Текст 3.**

**Modeling the Photocatalytic Process of Variation in Chemical Oxygen Demand *via* Stochastic Differential Equations**

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**Abstract**: Several papers in the literature on Advanced Oxidation Processes (AOPs) confirm the process as a viable alternative for the treatment of a variety of industrial effluents. In many of these works, modeling the variations of Chemical Oxygen Demand (COD) as a function of different experimental conditions was performed by techniques such as Design of Experiments, Artificial Neural Networks and Multivariate Analysis. These techniques require both a large number of parameters and a large quantity of experimental data for a systematic study of the model parameters as a function of experimental conditions. On the other hand, the study of Stochastic Differential Equations (SDE) is presently well developed with several practical applications noted in the literature. This paper presents a new approach in studying the variations of COD in AOPs *via* SDE. Specifically, two effluents, from the manufacture of paints and textiles were studied by combined treatment of the photo-Fenton process and catalytic ozonization.

**Keywords**: Modeling, Stochastic Differential Equations, Chemical Oxygen Demand, Photo-Fenton process, Ozonization.

**1. INTRODUCTION**

Chemical oxygen demand is an important parameter for

estimating the concentration of organic contaminants in water

supplies and industrial wastes. Since the degradation of

organic compounds demand oxygen, the concentrations of

these substances can be estimated by the amount of oxygen

required. A method using dichromate as the oxidizing agent

in a closed system is critical in determining COD due to dichromate’s

high oxidation potential and its operational ease

for a wide variety of sample types. Inorganic species such as

the O2

2-, Fe2+, halogens and SO2 have a reduction capacity,

especially for potassium dichromate, interfering positively in

test results. Also, the interference of chloride and nitrite is

preventable by the addition of mercuric sulfate and sulfamic

acid, respectively. However, a method correcting the interference

of inorganic species such as Fe2+ and H2O2 is not

mentioned in standard methods and is also poorly reported in

the literature [1].

Several industrial effluents are resistant to degradation by

conventional processes such as biological or physicalchemical.

Thus, advanced chemical oxidation processes

(AOPs) such as H2O2/UV, O3 and Fenton's reagent are very

promising techniques in industrial applications [2].

Advanced chemical oxidation processes are divided into

two groups: homogeneous and heterogeneous. The first

occurs in one step and uses ozone, hydrogen peroxide or

Fenton's reagent (a mixture of H2O2 with Fe2+ salt) as generators

of hydroxyl radicals. The second type uses semiconductors

as catalysts (titanium dioxide, zinc oxide, *etc*.) [3]. The

use of UV radiation and the semiconducting properties of the

catalyst allow for the formation of hydroxyl radicals and

subsequent oxidation of effluent.

**Химия. Текст 4.**

**Kinetic Models of Integrated Solidification and Cementation of Cementformation**

**Interface with New Method**

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**Abstract:** The isolation failure of cement-formation interface is an important and urgent problem in oil production, while

an effective way to solve it is to realize the integrated solidification and cementation of cement-formation interface (ISCCFI).

In order to study the kinetics of ISCCFI with MTA (Mud Cake to Agglomerated Cake) method, the Diamond Differential

Scanning Calorimetry Analyzer is adopted for experiments with dynamic method and isothermal method. The

results show that there is a linear relationship between the solidification reaction temperature and the heating rate of ISCCFI

with MTA method. For the first exothermic peak, the initial temperature, peak tip temperature and final temperature

are 53 °C, 69 °C and 83 °C respectively, and the apparent activation energy of solidification reaction is

44.39×10-3 kJ·mol-1, the natural logarithm of preexponential factor is 7.26, the solidification reaction order is 0.88. For

the second exothermic peak, the initial temperature, peak tip temperature and final temperature are 83 °C, 92 °C and

114 °C respectively, and the apparent activation energy of solidification reaction is 99.14×10-3 kJ·mol-1, the natural

logarithm of preexponential factor is 24.77, the solidification reaction order is 0.94. The maximum solidification reaction

rates at 50 °C, 75 °C and 90 °C are 0.09×10-3 s-1, 0.27×10-3 s-1 and 0.51×10-3 s-1 respectively. The kinetic models of

ISCCFI with MTA method under different temperatures are established. It provides a theoretical and technical support for the isolation improvement of cement-formation interface.

**Keywords:** Kinetic model, Fluid channeling, Cement-formation interface, MTA method.

**1. INTRODUCTION**

Along with the secondary development of old oilfields,

the oilfield development in China and even the world mainly

have two problems. First, the interlayer channeling after the

production of oil wells can cause watered-out reservoirs.

Second, the fluid magrition after well cementing can usually

cause the great danger. An origin of these problems is the

isolation failure of cement-formation interface, and it has

seriously restricted the effect and benefit of petroleum

exploration and development [1-4]. The practice proves that

the main pathway of fluid channeling is located in the cement-

formation interface [5]. In other words, the cement

sheath can be peeled off from the borehole wall so long as

the mud cake exists. This will cause microcracks between

cement sheath and borehole wall, which reduces the bonding

strength of cement-formation interface and provides a path

or channel for fluids (oil, gas and water) from the reservoir

or formation [6, 7]. So the main factor that causes the isolation

failure of cement-formation interface is the interface

defects [2]. In order to solve this problem, the MTC (Mud to

Cement) method was proposed in the early 1990s [8]. This

method can achieve the integrated solidification and cementation

of cement-formation interface (ISCCFI) combined

with multifunctional drilling fluids [9, 10]. However, it has

been questioned by many scholars since 1994, because the

MTC solidified body is brittle [11-13]. So, the MTC method

can only be used in the well cementing of surface casing and

intermediate casing of oil and gas well [14, 15].

**Химия. Текст 5.**

**Synergism of Mud Cake Modifier with Forming Agent of Agglomerated Cake at Cement-Formation Interface with MTA Method**

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**Abstract:** Based on the method of mud cake to agglomerated cake (MTA), the synergism of mud cake modifier (MCM) with forming agent of agglomerated cake (FAAC) in oil and gas well is studied by means of X-ray diffraction (XRD), environmental scanning electron microscopy (ESEM) and atomic absorption spectroscopy (AAS). The results show that the mud cake with MCM at cement-formation interface (CFI) is corroded by FAAC. And the corrosion spots and cracks are formed. The glassy substance in mud cake is depolymerized by hydrated ions from oilwell cement slurry through these spots and cracks. The soluble ionic groups in mud cake form. The diagenesis in mud cake at CFI occurs. The calcium silicate hydrates (CSH), ettringite, film zeolite, rod zeolite and natrolite gels in mud cake generate. Ultimately, it achieves the integrated solidification and cementation (ISC) among cement paste, agglomerated cake and formation at CFI. This paper explains why the isolation quality of CFI is improved by the MTA method.

**Keywords:** Mud cake modifier, Forming agent of agglomerated cake, Ion, Diagenesis, Synergism.

**1. INTRODUCTION**

The isolation failure of cement-formation interface (CFI)

is a main problem in well cementing of oil and gas wells [1],

because the integrated solidification and cementation (ISC)

among cement, mud cake and formation at CFI cannot be

achieved [2]. Based on this, a method of mud to cement

(MTC) emerged in the early 1990s [15]. By combining the

MTC method and multifunctional drilling fluids, ISC was

achieved. However, this method had been questioned by

many scholars [3, 4]. They argued that the MTC solidified

body was liable to the serious embrittlement. Thus the MTC

method can only be used in the well cementing of surface

casing and intermediate casing in oil and gas wells, as the

MTC solidified body does not have the solidified performance

of traditional oilwell cement [5].

Based on this, the new method of mud cake to agglomerated

cake (MTA) to improve the isolation quality of CFI was

proposed [6]. This method can be divided into two steps.

Firstly, the mud cake modifier (MCM) is added into the

drilling fluid before drilling to 50-200 m above the cementing

interval. The MCM addition is from 0.5 wt.% to 5.0

wt.%. Secondly, the spacer fluid (3 - 4 m3) is prepared with

forming agent of agglomerated cake (FAAC) [7]. Then this

fluid and cement slurry is injected into the well in turn. In

this new method, the cement slurry system is not changed.

The evidences of ISC at CFI with MTA method were obtained

[8, 9]. The kinetic models of ISC with MTA method were

established [10]. The application effects of five

oilfields in China showed the MTA method improves significantly

the qualified rate and high quality rate of well cementing

[11, 12]. Based on X-ray diffraction (XRD), environmental

scanning electron microscopy (ESEM) and atomic

absorption spectroscopy (AAS), the synergism of MCM with

FAAC was studied.