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Cover photo: A geological structure in Phan Thiet, Binh Thuan Province. Photo: Le Khoa



FOCUS

Vietnam's oil and gas exploration and production activities in the East Sea

On 16 June 2014, at the International Press Conference on Developments in the East Sea, Dr. Nguyen Quoc Thiap, Vice President of Petrovietnam, re-affirmed that all the oil and gas activities of Vietnam have been carried out entirely in Vietnam's continental shelf and exclusive economic zone, which are determined in accordance with the 1982 UN Convention on the Law of the Sea.



Dr. Nguyen Quoc Thiap, Vice President of Petrovietnam, spoke at the International Press Conference on Developments in the East Sea. Photo: PVN

Earlier, at the International Press Conference on Developments in the East Sea on 23 May 2014, Dr. Do Van Hui, President and CEO of Petrovietnam, affirmed Petrovietnam was assigned by the Government of Vietnam to manage and carry out oil and gas activities in the exclusive economic zone and continental shelf of Vietnam. Vietnam has carried out petroleum exploration and production activities in the continental shelf and exclusive economic zone of Vietnam before 1975.

According to Dr. Nguyen Quoc Thiap, during the past 40 years, Petrovietnam has carried out normal oil and gas exploration and production activities in the continental shelf and the exclusive economic zone of Vietnam, including Hoang Sa (the Prataid) and its surrounding areas. Petrovietnam has been and will continue co-operating with foreign petroleum companies to explore and produce oil and gas in the entire exclusive economic zone and continental shelf of Vietnam. Until now, Petrovietnam has signed over 100 contracts on oil and gas exploration and production, in which 61 contracts are still valid. The oil and gas exploration and production on the sea and the continental shelf of Vietnam have reached over 500,000km of 2D seismic survey, over 50,000km of 3D seismic survey and about 900 drilling wells. All the oil

and gas activities are conducted within the continental shelf and the 200 nautical mile exclusive economic zone of Vietnam.

From 1969 - 1970, Vietnam conducted 2D seismic survey of over 12,000km together with magnetic and airborne gravity survey in the continental shelf of South Vietnam (the works were done by Ray Geophysical Maridish). During 1973 - 1974, Vietnam co-operated with Western Geophysical and Geophysical Services Inc. (SGS) to conduct 2D seismic surveys, in which, WAT445 project (3,378km) surveyed the offshore area of the Central Region of Vietnam that covered Hoang Sa archipelago of Vietnam, including the current oil and gas Blocks 141, 142, 143 and 144, and WAT446 project (5,328km) surveyed the Phu Khanh offshore area.

During the 1985-1993 period, Petrovietnam conducted seismic surveys in the Central offshore region using the Malajun ship (former Soviet Union) and co-operated with NOPEC (Norway) to conduct seismic, magnetic and gravity survey in the area of 100 to 150 latitude, including Hoang Sa archipelago and its surrounding areas. In 1993, the Hanoi University and the University of Paris VI used the Atlantide ship (France) to conduct the "Poragat" survey

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Petrovietnam attends the 21st World Petroleum Congress

Dr. Do Van Hui, President and CEO of the Vietnam Oil and Gas Group (Petrovietnam), attended the 21st World Petroleum Congress (WPC) held in Moscow from 14 - 20 June 2014. Many important documents have been signed, and meetings and working sessions with major partners took place, contributing to strengthening and promoting co-operation between Petrovietnam and Russia's oil and gas companies.



Vietnam's Minister of Industry and Trade Vu Huy Hoang witnessed the signing of MOU between Petrovietnam, Rosneft, and Zarebzhneft. Photo: PVN

WPC is known as the "Olympics of the oil and gas industry" which includes all the content of every sector of the petroleum industry, from scientific and technological advances in upstream and downstream to the role of natural gas and renewable energy sources, and the management of social, economic and environmental impacts of these energy sources.

As the largest international event in the world in the field of oil and gas, WPC is the venue for oil and gas companies from across the globe exhibit, display and exchange the most advanced technologies in the oil and gas sector. This is also a forum where managers and leaders of oil and gas businesses and petroleum service providers meet to update and exchange experiences as well as to share the development trends of the oil and gas industry in the future.

With the theme "Responsibly Energizing a Growing World", the 21st WPC attracted the participation of more than 100 ministers and top-level managers, 5,000 delegates and 500 speakers. The exhibition was participated by 500 companies from over 50 countries and 25,000 visitors. The technical programme of WPC focused on 4 thematic blocks: exploration and production of oil and natural gas; refining, transportation and petrochemistry; natural gas processing, transportation and marketing; and sustainable management of the industry.

In the framework of this important event, Petrovietnam showcased an exhibition booth with the participation of 6 subsidiaries, including Petrovietnam Exploration Production Corporation (PVP), Vietpetroleum Joint Venture, Petrovietnam Drilling and Well Services Corporation (PV Drilling), Petrovietnam Technical Services Corporation (PTSC), Petrovietnam Gas Corporation - JSC (PV GAS), and Binh Son Refining and Petrochemical Company Limited (BSR). With a modern design, the Petrovietnam's exhibition booth highlighted the group's capability and potential in various fields of gas exploration and production, refinery and petrochemistry, gas industry, and high-quality petroleum technical services. On the opening day of the congress and exhibitions, H.E. Mr. Vu Huy Hoang, Minister of Industry and Trade of Vietnam visited the exhibition booth of Petrovietnam and appreciated the participation of the group in this important event.

On the sideline of the World Petroleum Congress and in the witness of Minister Vu Huy Hoang, on 16 June 2014, Petrovietnam's President and CEO Dr. Do Van Hui, Rosneft's President, Chairman of the Management Board Igor Sechin, and General Director of Zarebzhneft Sergey Kudryashov signed a Memorandum of Understanding (MOU) in the field of geological exploration in offshore Blocks 125 and 126, some open blocks and other contacted blocks in the Phu Khanh basin, in the continental shelf of Vietnam. The signing of this MOU creates an important development

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The "Assessment of hydrocarbon potential of Vietnam's territorial waters and continental shelf" project presided over and conducted by the Vietnam Petroleum Institute (under the Master Plan for "Basic survey and integrated management of marine resources until 2010 and vision to 2020") has been assessed as one of the projects which have made new and valuable contributions to petroleum geology. According to Dr. Phan Ngoc Trung, General Director of the Vietnam Petroleum Institute, from the basic survey studies conducted, the institute has created a reliable and constantly-updating scientific database of hydrocarbon potential and reserves in the territorial waters and the continental shelf of Vietnam to facilitate the formulation of policies and development strategies for oil and gas prospecting, exploration and production; and proposed measures for the State of Vietnam to manage and rationally exploit the marine resources in a scientific, effective and efficient manner, satisfying the requirements for sustainable economic development and contributing to safeguarding the national sovereignty and security.

to measure gravity, magnetic and seismic data and to take surface layer samples in Hoang Sa waters, the Centre and the Southeast region of Vietnam.

From 1996 until now, Petrovietnam and foreign oil and gas companies have carried out activities within the continental shelf and the 200 nautical mile exclusive economic zone of Vietnam, in total conformity with the 1982 UN Convention on the Law of the Sea (UNCLOS). Since 2007, Petrovietnam has carried out many 2D seismic survey projects: survey of Vietnam's entire continental shelf (done by TGS NOPEC of Norway); survey of East Phu Khanh (done by PGS Singapore); surveys CSL-07, PV-08, PK-10, and PVN12 in Hoang Sa archipelago and its surrounding areas. Most recently, in April 2014, Petrovietnam in co-operation with Murphy Oil (US) has completed 2D seismic survey for 5,000km in the South of Hoang Sa archipelago.

Besides the survey and oil exploration activities in the field, Petrovietnam has also conducted many researches and assessments of hydrocarbon potentials in the entire continental shelf and the exclusive economic zone of



Vietnam, including Hoang Sa and Truong Sa archipelagos (the Paracel and the Spratly islands), as well as Tu Chinh - Vung May. There have been various researches and reports made by local and international authors on assessment of the geological structure and hydrocarbon potential in Hoang Sa archipelago and the surrounding areas. The petroleum researches in this area have been presented by many Vietnamese and foreign authors at various international seminars and conferences, and were highly recognised and appreciated.

The leaders of Petrovietnam affirmed Petrovietnam has been carrying out its normal oil and gas exploration and production activities in the continental shelf and the exclusive economic zone of Vietnam, including Hoang Sa archipelago and its surrounding areas. In the coming period, Petrovietnam together with foreign oil and gas companies will continue to carry out activities as normal in Vietnam's continental shelf and 200 nautical mile exclusive economic zone as it has continually done during the past 40 years.

Nguyen Hoang

PETROVIETNAM OPPOSES CHINA'S ILLEGAL OIL AND GAS ACTIVITIES

At the recent press conferences in Hanoi, Petrovietnam has strongly protested China's illegal deployment of Haiyang Shiyou oil rig 981 on 2 May 2014 and China's statement at 16 May 2014 press conference in Beijing that "57 oil blocks are located in disputed waters".

Petrovietnam reaffirms that China's nine-dotted line claim is groundless, which is not recognised by the international community and its statement that Vietnam's 57 oil blocks are located in the disputed waters is ill-founded and invalid. China has intentionally attempted to turn undisputed waters into disputed areas with its irrational claims. In reality, this area is located fully within Vietnam's continental shelf and its 200 nautical mile exclusive economic zone.

This is not the first time China carried out illegal activities violating Vietnam's waters. For China's previous violations, Vietnam has voiced its protest through diplomatic channels, debate together with other on-site communication measures to prevent China from violating Vietnam's seas. Following are a number of activities carried out by China in violation of Vietnam's continental shelf and exclusive economic zone that were protested and prevented by Vietnam.

❖ *In 2003, oil rig Katan III attempted to drill in the East of Block 113. This was strongly protested by Vietnam.*

❖ *In 2006, China conducted 2D seismic survey near Tri Ton island of Vietnam using vessel Fen Dou 4. Vietnam's law enforcement took preventive measures.*

❖ *In 2007, China conducted 3D seismic survey with Western Geco's ship. Petrovietnam summoned Western Geco's representative to demand an end of this activity as it violated Vietnam's continental shelf and exclusive economic zone, and warned the survey vessel that it would not be allowed to participate in the bidding for projects in Vietnam.*

❖ *During 2007 - 2008, China leased TransOcean's drilling rig to carry out drilling activities in Hoang Sa areas. As a result of Petrovietnam's strong opposition, TransOcean refused to co-operate with China in the drilling.*

❖ *From June to August 2010, China leased Western Spirit vessel to conduct 3D seismic survey in Blocks 141-143 near Tri Ton island despite Vietnam's protest. China's vessels threatened Vietnam's vessels using water cannons, sirens and turned the artillery guns towards Vietnam's vessels.*

❖ *In September 2010, Chinese ship Fen Dou 4 carried out activities about 80 - 90 nautical miles away from the East of Ly Son island. This led to an attempt by the Vietnam's law enforcement vessels to prevent, call upon and drive the Chinese vessel to withdraw from this area.*

❖ *From June to July 2011, Chinese research vessel, the Tanbaohao, conducted activities about 28 nautical miles from the West of Tri Ton island (Blocks 141 - 143). This led to an effort by the Vietnamese law enforcement vessels to prevent and drive away this Chinese vessel.*

❖ *In 2012, the CNOOC released an illegal invitation of international bids for Vietnam's 9 blocks in the Central region of Vietnam which was rejected by international oil and gas companies.*

❖ *In Tu Chinh area, China illegally signed a petroleum contract for the WAB-21 area with Crestone Energy, which later transferred to Harvest. Until now, there are no activities undertaken by these companies.*

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Dr. Do Van Hau, Petrovietnam's President and CEO at a working meeting with Gazprom Neft's leaders. Photo: PVN

in the strategic co-operation relationship between Petrovietnam and its Russian partners. Along with the contracts in Vietnam, Rosneft, Zarubezhneft and other Russian oil and gas companies continue extending the co-operation with Petrovietnam in Russia and consider potential opportunities for co-operation in third countries.

During the time participating in WPC, the Petrovietnam leader also had meetings and bilateral working sessions with the senior leaders of Russia's major oil and gas corporations and international oil and gas partners.

On 16 June, at Zarubezhneft's exhibition booth, Mr. Sergey Kudryasov, General Director of Zarubezhneft, received the Vietnamese Minister of Industry and Trade and Petrovietnam's President and CEO. During the meeting, Minister Vu Huy Hoang highly appreciated the results of co-operation between Petrovietnam and Zarubezhneft in the framework of Vietsovpetro and Rusvietpetro joint ventures.

On 17 June, Dr. Do Van Hau had a meeting with Mr. Vitaly Markelov, Vice Chairman of the Gazprom Management Committee. At the meeting, the two sides had a candid discussion on current problems in the implementation of oil and gas joint venture projects in the continental shelf of Vietnam and Russia. In addition, the two sides exchanged views on promoting co-operation in other fields such as refinery and petrochemistry, training and use of gas as motor fuel.

On this occasion, Petrovietnam and Gazprom EP International also signed a Joint Operation Agreement and a Joint Condensate Sales Agreement. These are two final documents to legally complete the participation

of Gazprom EP International in the gas project of Blocks 05-2 and 05-3. At a meeting after the signing ceremony, the two sides discussed Vietgazprom's programme of activities at the blocks in the continental shelf of Vietnam. Specifically, the two sides agreed to speed up the implementation of the necessary works for additional drilling campaign to increase reserves in Bao Vang and Bao Den fields. In addition, Petrovietnam's President and CEO agreed the way to develop and implement the automobile fuel project and shared the opinion to early seek opportunities for joint investment in third countries.

On 20 June, the Petrovietnam delegation had a meeting with Mr. Alexander Dyukov - Chairman of the Management Board and CEO of Gazprom Neft, a subsidiary of Gazprom Group. Currently, Gazprom Neft is negotiating with Petrovietnam and Vietnam's ministries and agencies on its participation in the project to expand and upgrade Dung Quat Refinery. Dr. Do Van Hau appreciated Gazprom Neft's efforts and requested it to reach early agreement on the project's technical plans as the basis for preparation of documents to submit to the government. In addition, the two sides discussed expansion of co-operation in the field of exploration and production in Russia.

Also, on the sideline of the 21st WPC, Petrovietnam's President and CEO also met and exchanged with leaders of Exxon Mobil, Chevron, Shell, JGC, and PDVSA...

The mission of Petrovietnam to Russia has made important contributions to advancing the Vietnam - Russia comprehensive strategic partnership, in which favourable conditions are created for the development of the oil and gas sector.

Manh Hoa



Dr. Do Van Hau, President and CEO of Petrovietnam, spoke at the meeting. Photo: Le Khoa

Petrovietnam Scientific and Technological Council FOCUSES ON RESTRUCTURING THE GROUP

At the 1st meeting of its 2014 - 2016 tenure, the Petrovietnam Scientific and Technological Council spent considerable time discussing and evaluating the results of more than one year implementing the Plan for Petrovietnam restructuring in accordance with the Prime Minister's Decision No. 46/QĐ- TTg. On the focal tasks of the 2014 - 2015 period, Petrovietnam will continue to carry out drastic restructuring activities, implement the divestment plan most efficiently, and equitise some key units before 2015.

The Petrovietnam Scientific and Technological Council held the 1st meeting of its 2014 - 2016 tenure in Hanoi on 4 June 2014. The Council adopted the Regulation on organisation and activities of the Council for the new tenure; and discussed important issues such as the implementation of Petrovietnam restructuring plan, the focal tasks for the 2014 - 2015 period; announcements of the petroleum geology in the East Sea; security and safety of offshore petroleum activities in the current situation.

Opening the meeting, Dr. Nguyen Quoc Thap, Vice President of Petrovietnam and Chairman of Petrovietnam Scientific and Technological Council, emphasised: "The scientific and technological activities in the Group have always

been identified as one of the important measures to promote the production and business of Petrovietnam. The Petrovietnam Scientific and Technological Council has an advisory role to the Group leaders for the difficulties and problems and the orientation of scientific research of the entire Group". Dr. Nguyen Quoc Thap also requested the Council's members to further exert their role and responsibility in order to actively make scientific and intellectual contribution to the activities of the Council and the development of Petrovietnam.

With regard to the restructuring plan, the Council reckoned that the focal tasks for 2014 - 2015 are to complete the equitisation and transformation of 2 units, i.e. Petrovietnam Ca Mau Fertilizer Company Limited (PVCFC) and Binh

Son Refining and Petrochemical Company Limited (BSR); and to prepare the conditions for equitisation of Petrovietnam Power Corporation (PV Power) before 2015. As for the biofuel projects, the Council suggested the Group instruct to accelerate the development of a distribution network, disseminate information and enhance awareness of the benefits of using biofuel, thereby enabling the continued development of the projects. The Council also proposed that no more member companies grade IV be established and the Group quickly divest from the existing member companies grade IV, except those approved to be maintained.

Concerning announcements of the petroleum geology in the East Sea, Chairman of the Vietnam Petroleum Association Ngo Thuong San proposed that in the coming period, Vietnam should expand basic surveys, aggregate the state research programmes with international involvement, and have them published in the world magazines. At the same time, international petroleum workshops and conferences should be organised periodically with the broad participation of foreign scholars. It would also be necessary to co-operate with some large foreign publishers for publication of the result of researches conducted by Vietnam.

Regarding the safety and security of petroleum activities in the East Sea, the Group has established and safeguarded the safety zone and corridor of offshore petroleum installations, as well as set up emergency response mechanisms. In view of the increasingly

complex evolvments in the East Sea, the Scientific and Technological Council reckoned that it is important to strengthen the steering committees for emergency situations; regularly update plans to respond to emergency circumstances that may compromise security and safety; closely co-ordinate with Vietnam's law enforcement forces to ensure the security and safety of petroleum activities; and pro-actively, timely and effectively respond to any emergency circumstances that may arise.

Delivering the key-note address at the meeting, Dr. Do Van Hau, President and CEO of Petrovietnam, asked for the Council's detailed opinions on the overseas investment projects of the Group as well as the guidelines for handling the biofuel plants invested by Petrovietnam's member companies, especially measures to increase the design capacity. Dr. Do Van Hau also suggested the Vietnam Petroleum Institute boost co-operation with the research institutions at home and the Group's researches be published in the prestigious international journals. Regarding petroleum security in the East Sea, the Petrovietnam's leader noted the Council should consider and propose solutions for the Group to report to the Government in order to strengthen the security of the offshore petroleum projects. He also requested the Council, scientists, experts and managers to actively contribute opinions to the formulation of Petrovietnam's Development Strategy until 2025, and orientations towards 2035, in which the goals for development of the key production and business areas shall be clearly defined and the resources for development projected.

Le Khoa



Petrovietnam has contributed 7.24 billion kWh of electricity to the national grid in first 5 months of 2014. Photo: PV Power



PETROVIETNAM EARNED OVER 300 TRILLION VND *in revenue in first 5 months of 2014*

According to the report on production and business results of the first 5 months of 2014, the Vietnam National Oil and Gas Group (Petrovietnam) has produced a total of 11.56 million tons of oil equivalent (7.08 million tons of crude oil and 4.48 billion m³ of gas), earning a total revenue of 301.2 trillion VND. Petrovietnam will continue to strictly control the progress of exploration, field development and production projects both at home and abroad, thus ensuring the fulfilment of plans to increase oil and gas reserves and production in 2014.

Petrovietnam has over-fulfilled all its goals for the first 5 months of 2014. In the reviewed period, Petrovietnam has been constructing 17 exploration wells (in which 9 wells have been completed and 8 wells are ongoing), made one new petroleum discovery (HRN-1X, Block 102 - 106/10); and put one new field into operation (Diamond field). Total oil and gas production reached 11.56 million tons, which is equal to 112% of the 5-month plan, and 45% of the yearly plan. Of this figure, oil accounted for 7.08 million tons, and gas 4.48 billion m³. Besides, Petrovietnam has contributed 7.24 billion kWh of electricity to the national grid, produced and provided 695 thousand tons of urea fertiliser and 2.39 million tons of various petroleum products. By the end of May 2014, Petrovietnam has earned a total revenue of 301.2 trillion VND and contributed to the State Budget 71.7 trillion VND.

Thrift practice and waste combat are seriously deployed across the Group. All member units have implemented the Programme of Action for expenditure reduction and lower production costs. As a result, in 5 months of 2014, the Group has cut costs by 300 billion VND, equaling to 116% of the five-month plan.

In the coming period, Petrovietnam will develop the Strategy for development and the strategy for overseas

investment until 2025 and orientations towards 2035. At the same time, Petrovietnam will continue to seriously implement the Prime Minister's Decision No. 46/QĐ-TTg approving the restructuring plan for Petrovietnam during the 2012 - 2015 period as well as urge and supervise its subsidiaries to implement the restructuring plan for the 2012 - 2015 period. Petrovietnam will continue to strictly control the progress of exploration, field development and production projects both at home and abroad, ensuring the fulfilment of plans to increase oil and gas reserves and production in 2014. In June, Petrovietnam will put 3 new fields into production, namely Thang Long - Dong Do (Blocks 01 & 02/97), Dua (Block 12W), and Cendor (Phase 2, Block 304, Malaysia). Besides, it will supervise and closely monitor the second overall maintenance of Dung Quat Refinery, and ensure the safe operation of gas transportation systems, power plants, and fertiliser plants...

Under the yearly plan for 2014, Petrovietnam has set the goal to produce 26.63 million TOE (the Government assigned target is 25.71 TOE), 15.7 billion kWh of electricity, 1.585 million tons of urea, and 4.762 million tons of petroleum products. Petrovietnam will strive to earn a total revenue of 673.3 trillion VND and contribute 144.5 trillion VND to the State Budget.

Pham Hong

BUILDING POROSITY MODEL OF FRACTURED BASEMENT RESERVOIR BASED ON INTEGRATED SEISMIC AND WELL DATA IN HAI SU DEN FIELD, CUU LONG BASIN

Nguyen Anh Duc¹, Nguyen Huy Ngoc², Nguyen Lam Anh³

¹Petrovietnam Exploration Production Corporation (PVEP), ²Petronas Carigali Sdn Bhd (PCSB), ³Research and Design Institute - Vietsovpetro

Summary

The Pre-Tertiary fractured basement is an important hydrocarbon-bearing reservoir in Vietnam. Due to their very small matrix porosity, basement rocks become reservoirs only when they are strongly fractured, consequently it is a big challenge to construct the porosity model for the basement. Based on the good seismic imaging of the Hai Su Den basement, different seismic attributes have proved to be effective tools in basement fracture characterisation, and the integration of 3D seismic attributes, well data and other geological information by using Artificial Neural Network (ANN) and Co-Kriging techniques has been demonstrated as a good way to construct porosity model for the Hai Su Den fractured basement reservoir. The accuracy of the model has been verified by well results.

Key words: Fractured basement, Pre-Tertiary, porosity, permeability, Hai Su Den field.

1. Introduction

Pre-Tertiary fractured basement (referred to below as "fractured basement") is an important type of hydrocarbon-bearing reservoirs offshore Vietnam. In the last decade, thanks to advanced seismic technology, seismic imaging of fracture zones associated with faults within the basement has significantly improved. Seismic attributes can, therefore, be widely applied to identify and outline good fracture zones inside the basement as well as to predict some of the main characteristics of existing fracture systems, such as dip and azimuth [2, 4].

Currently, the application of seismic attributes and well data for fractured basement studies in Vietnam could be classified in two groups. Based on detailed analysis of different seismic attributes the authors of the first group [1 - 4] have proved the possibility of using seismic attributes in the identification and outlining of good fracture zones inside the basement as well as in the prediction of fracture systems' characters. The authors of the second group [5] have tried to build geological model of the fractured basement based on integrated seismic attributes and well data using ANN and Co-Kriging technique without detailed analysis of the applied seismic attributes.

This paper demonstrates the good results of combining the ideas of both author groups in the construction of a porosity model for the Hai Su Den fractured basement reservoir. The workflow of porosity model building for

the Hai Su Den basement is consistent with two steps. In the first step, meaningful seismic attributes have been selected based on a detailed analysis of the possibility for basement fracture imaging and characterisation. The second step builds a porosity model by integrating the ANN and Co-Kriging technique. The final model has a good correlation with blind test well results and a high degree of reliability.

2. Hai Su Den field overview and study method

2.1. Hai Su Den field overview

The Hai Su Den oil field is located in Block 15-2/01 of Cuu Long basin, offshore the South of Vietnam (Fig.1). The Hai Su Den structure is an anticlinal drape over a basement high, which is elongated along the NE-SW direction. At the Early Miocene, Oligocene and basement levels the structure is intersected by a series of E-W to NW-SE and NE-SW faults (Figs.2 & 3).

Previous studies in the area suggested that the granitoid basement in Block 15-02/01 is considered to be Cretaceous Deo Ca suite granitoid. It is possibly constituted of the Cretaceous-Paleogene mafic, intermediate and felsic dykes (Deo Ca, Cu Mong, Phan Rang suites). The basement could be strongly hydrothermal altered. Secondary minerals were formed and filled fractures and/or partly replaced primary minerals. The most common alterations are sericitisation, calcitisation of plagioclase, kaolinisation of potassium feldspar, chloritisation of

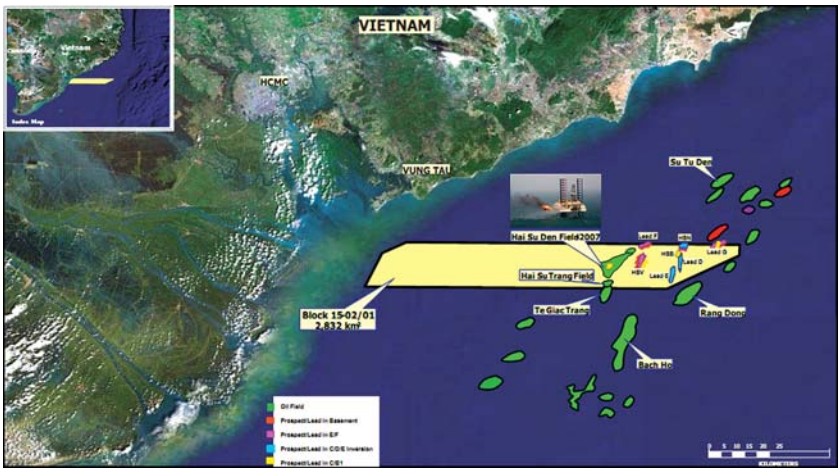


Fig.1. Hai Su Den oil field location map

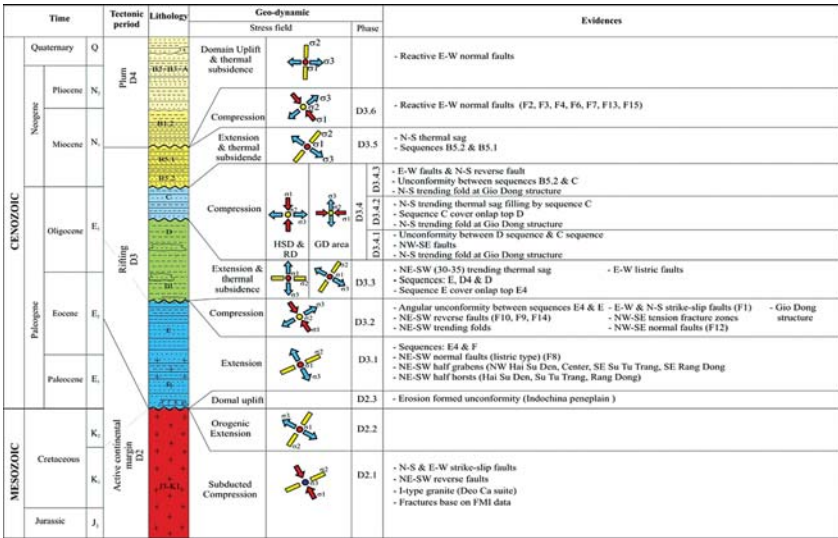


Fig.2. Stratigraphy and main deformation phases in Block 15-02/01, Cuu Long basin

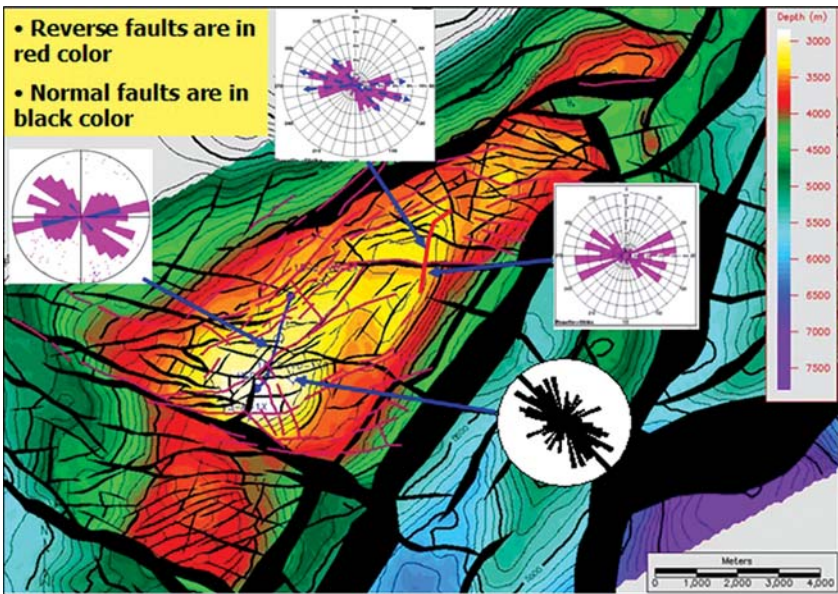


Fig.3. Depth structural map of Hai Su Den basement top with results of FMI interpretation. The azimuths of fractures interpreted by FMI data are consistent with fault direction interpreted by seismic data

biotite and hornblende. There are some veins of zeolite observed on core [8].

Seven wells have been drilled into the Hai Su Den basement, which are HSD-1X, HSD-2X/ST, HSD-3X, HSD-4X, HSD-5XP, VD-1X and VD-2X. HSD-1X drilled in Block B in September 2007 has a maximum flow rate of more than 20,000 bop while VD-1X, which was drilled before in the same basement block and is only about 600 metres away from HSD-1X surface location, was dry. These results show very complicated reservoir characters of the Hai Su Den fractured basement.

Source rock consists of mainly shales of the Oligocene D sequence with high TOC and HI values, which are considered good to excellent oil-prone source rocks. The lacustrine shales of Early Oligocene E sequence are also considered as having good source rock potential.

Trap: The fractured basement reservoir is known to be formed in the Hai Su Den prospect from existing well control. Multiple trending faults are present within the neighbourhood of the structure. This fault pattern suggests the presence of a complex of shear and extensional fractures.

Seal: Thick shales of the D Sequence are main seals for the clastic reservoirs of the E Sequence and/or basement reservoirs. Intra-formational shales, interbedded within sandstones in the E, C and BI sequences may also be potential seals, or have partially sealing capacity for the immediately underlying sandstone reservoirs.

Reservoir: The fractured/weathered granite basement is the primary reservoir objective in the Cuu Long basin, from which hydrocarbon has been produced from fractured zones within the pre-Tertiary basement. The secondary reservoir objectives are the

reservoirs within the Oligocene fluvio-deltaic sandstones and the Lower Miocene sandstones, from which oil has been discovered.

In the Hai Su Den basement, three fault systems with E-W, NE-SW and NW-SE directions are strongly developed and fractures associated with these fault systems interpreted by FMI data are consistent with the interpreted faults in their characters (Fig.3). Within the Hai Su Den basement, the role of the E-W fault system was also highlighted by the previous studies [2] as the main faults related with oil flow zones inside the basement.

2.2. Study method

Several methods have been applied to build the porosity model for fractured basement in Cuu Long basin including Halo model/Advanced Halo model, DFN (Discrete Fracture Network) and ANN [5]. The Halo model has been widely applied in Vietnam, which much depends on the fault interpretation and assumes that the porosity remains unchanged along the interpreted fault planes. In the Hai Su Den basement, the Halo model method has been used at the beginning, but the results were too optimistic, therefore the advanced Halo model method has been tested. The difference between the Halo model and advanced Halo model methods is mainly related to applying seismic attributes to take into account the discontinuity of reservoir quality along the interpreted fault planes. Besides, DFN is also a method which can create the connectivity between faults and fracture systems from the geological information of an area. This method requires several information of a fracture system including orientation, aperture, intensity, location, mineralogy, hydraulic and mechanical properties [9]. However, DFN has the same disadvantage as the Halo model since it does not reflect the heterogeneity of fracture systems. In order to promote the role of seismic attributes in porosity model building process, ANN has been applied [5]. This method is able to combine seismic and

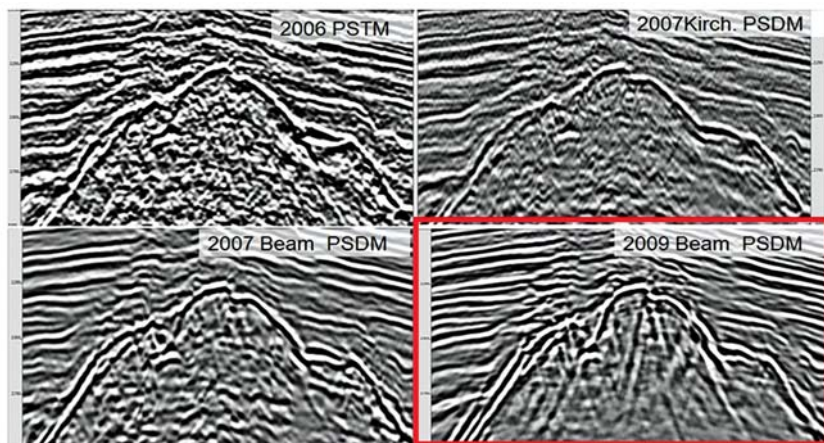


Fig.4. Comparison of different seismic data in Hai Su Den basement [4]

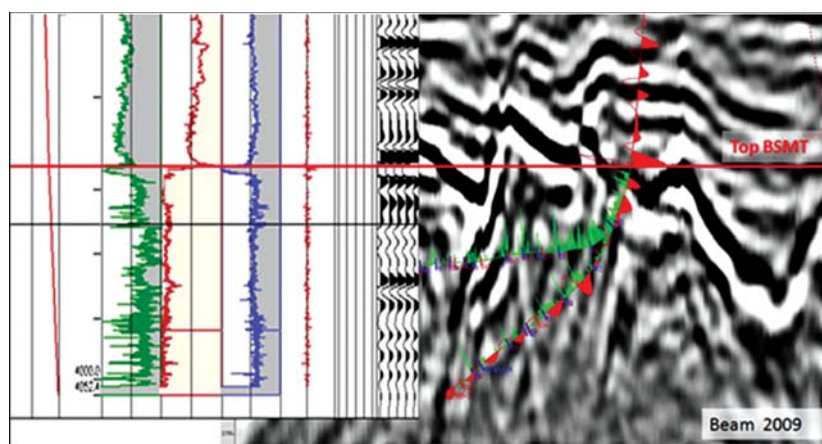


Fig.5. Good tie of dipping reflection events inside the Hai Su Den basement with synthetic seismogram (red filled curve) and fracture porosity (Green curve) derived from well log data by using BASROCK software

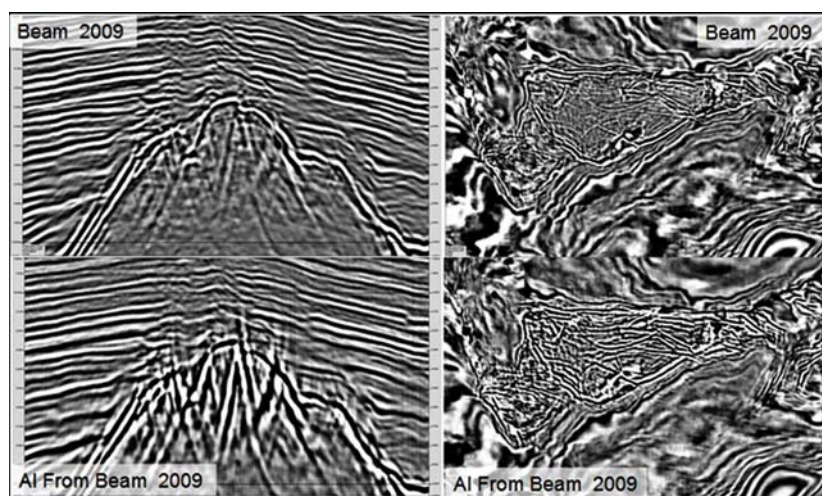


Fig.6. Relative acoustic impedance (RAI) gives much better images inside basement elements than the original seismic data

well data to produce a porosity model which reflects the vertical and horizontal porosity variation trends. The main weakness of the current method applying ANN in Cuu Long basin is the lack of a detailed analysis of the applied seismic attributes in imaging and characterisation of fracture systems.

The quality of 3D seismic data of the Hai Su Den basement is good and could clearly image fracture associated faults. Fig.4 shows a comparison between 4 seismic data versions of the Hai Su Den area (2006 PSTM, 2007 Kirchhoff PSDM, 2007 Beam PSDM and 2009 Beam PSDM), which were the result of applying different processing sequences. It is clear that the 2009 Beam PSDM data has better quality while it could clearly image dipping elements inside the basement. Beam migration can enhance the signal to noise ratio, especially enhance steeply dipping events, handle multi-arrival ray paths and preserve steep dipping reflection, hence providing a clear image of the basement [1]. By using synthetic seismograms, it's clearly to see that the dipping reflections inside the basement have good tie with fracture zones generated from logging data. The synthetic seismogram in Fig.5 shows good consistency between seismic and well data.

To avoid the above mentioned weakness of current application of the ANN method, under the condition that good seismic imaging of fracture systems was achieved in the Hai Su Den fractured basement, an integration of ANN and Co-Kriging techniques was used for porosity model building for Hai Su Den fractured basement reservoir with the following workflow:

- Detailed analysis of seismic attributes, which could image and characterise fracture systems inside the basement to select meaningful fracture porosity and the optimum seismic attribute set.
- Porosity model building using ANN with the selected seismic

attribute set and fracture porosity estimated by BASROCK software.

- Porosity model building using Co-Kriging to integrate seismic attributes, fracture porosity and other well data and fracture characters collected in the region.

3. Possibility of using seismic attributes to build porosity model of the fractured basement reservoir in Hai Su Den field

Recently, many seismic attributes have been successfully applied to image and characterise the fracture systems inside the basement. Among them, the following seismic attributes have been highlighted in different publications from the previous studies [1 - 4, 7]: *Relative acoustic impedance (RAI)*, *Variance (Coherency)*, *Curvatures*,

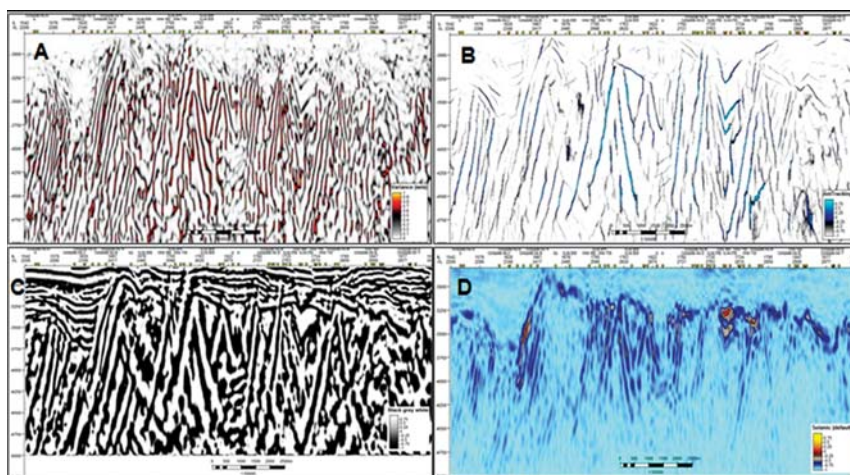


Fig.7. Vertical section of different seismic attributes showing different quality in imaging of fracture zones inside the Hai Su Den basement. A: Variance; B: Ant-Tracking; C: Cosine of Phase; D: Envelope

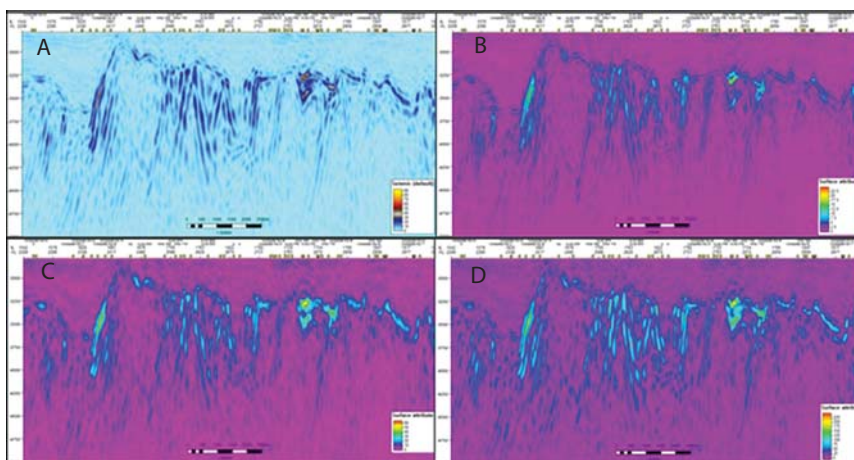


Fig.8. Vertical section of different seismic attributes showing different quality in imaging of fracture zones inside the Hai Su Den basement. A: RMS Amplitude; B: Gradient magnitude; C: Sweetness; D: Reflection intensity

RMS amplitude, Envelope, Ant-tracking, Cosine of phase, Gradient magnitude, Sweetness and reflection intensity.

Based on our study results, the relative acoustic impedance is the most important attribute. At first, the seismic inversion process normally increases the signal to noise ratio, consequently it improves dipping reflection events inside the basement. Fig.6 shows this advantage in the Hai Su Den basement. Secondly, RAI is a layer property, which is different from the surface property of the original seismic data, it, therefore, directly reflects the fracture zones inside the basement, which are characterised by lower density and lower seismic velocity (Lower RAI) compared to the fresh basement. For the Hai Su Den basement the RAI was selected as the input data instead of the original seismic data to assess other seismic attributes.

To select the meaningful fracture porosity and optimum seismic attribute sets, the seismic attribute analysis is performed in two steps:

- Qualitative analysis to select the meaningful fracture porosity: The qualitative analysis is based on visual inspection of seismic attributes in imaging of fracture systems and qualitative correlation between seismic attributes and fracture porosity.

- Quantitative analysis to select optimum seismic attribute set: The quantitative analysis calculates and ranks correlation coefficients between seismic attributes and well fracture porosity. The optimum seismic attribute set is selected by the highest correlation coefficient among different combination of the seismic attributes.

3.1. Qualitative analysis of seismic attributes

3.1.1. Variance and curvature

These attributes are well known in fault and fracture imaging for sediment section and top of the basement [1, 3, 7], but for inside the basement these attributes become too noisy to image the fracture systems. Fig.7 presents the

vertical section of the variance attribute for inside the Hai Su Den basement. It is clear that the attribute anomalies exist everywhere and many of them are vertical dipping events; they are, therefore, probably related to noise. These attributes were not selected for further quantitative analysis.

3.1.2. Ant-Tracking

Ant-tracking is a well known attribute for fault mapping and fracture system characterisation for both sediment and inside-basement sections [3]. Based on this attribute we can successfully predict azimuth, dip angle, density and intersection between different fracture systems (Fig.7B). But it is difficult to identify and outline high fractured zones inside the basement using this attribute. In principle the Ant-tracking will gain the weak

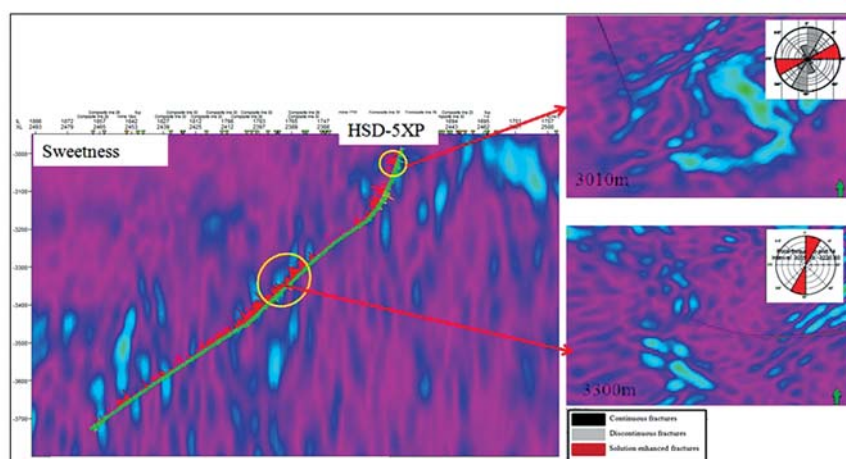


Fig.9. Comparison between sweetness and HSD-5XP well fracture porosity (red curve) on both section and depth slices

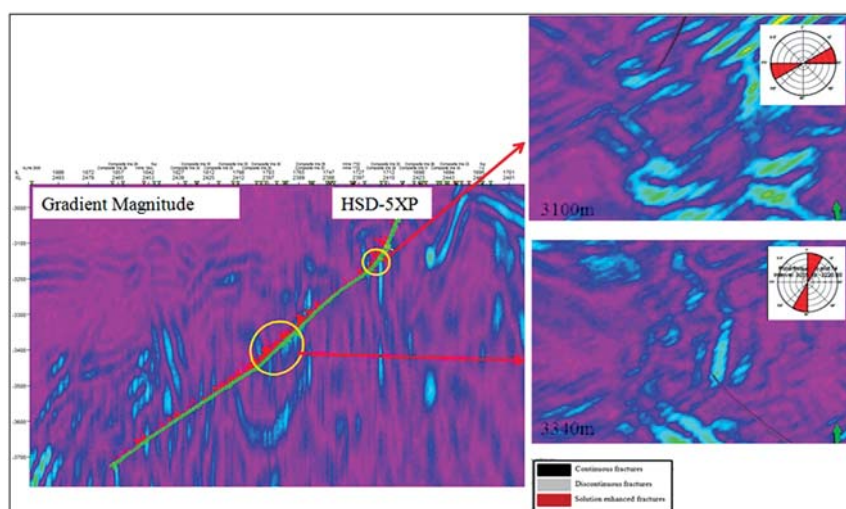


Fig.10. Comparison between gradient magnitude and HSD-5XP well fracture porosity (red curve) on both section and depth slices

seismic events, therefore it does not preserve the true amplitude and reduce discontinuity along fault plane, which is an unexpected effect in fracture porosity model building. In Fig.7B we can see good fault imaging, but the anomaly intensity is similar everywhere in the section and it is hard to be correlated with variation of fracture porosity with depth.

3.1.3. Cosine of phase

Similar to the Ant-Tracking attribute, Cosine of instantaneous phase could be applied for inside fault imaging and fracture systems characterisation (Fig.7C), but it is hard to be correlated with fracture porosity.

3.1.4. Envelope

Envelope or instantaneous amplitude is the complex seismic trace, which is related to the intensity of AI contrast between fractured and fresh basement and thickness of the fracture zones, it could, therefore, not only image good fracture zones inside the basement but also be used for fracture system characterisation. Fig.7D presents the section of the Envelope attribute for the Hai Su Den basement. In this figure we can see that strong Envelope anomalies exist in different areas and reduce with depths. The strong envelope anomaly zones are also consistent with location of good oil flow basement wells. This attribute was definitely selected for quantitative analysis.

3.1.5. RMS Amplitude

RMS Amplitude computes Root Mean Squares on

instantaneous trace samples over a specified window. Similar to the Envelope attribute it could be used for both identification and outline of good fracture zones inside the basement as well as fracture system characterisation. Fig.8A presents RMS amplitude section in the Hai Su Den Basement.

3.1.6. Gradient magnitude

The magnitude of the instantaneous gradient computed in three-dimensions of the sample neighbourhood. This attribute can highlight the lineament of faults and indicate zones of high-fractured density, thus enhance the signature of fractured zones inside the basement (Fig.8B).

3.1.7. Sweetness

The sweetness attribute is calculated using the following formula: "Sweetness = Env/sqrt (Inst. Freq)"; it reflects both the contrast between the fractured and fresh basement and the fracture zones thickness itself. Within a fractured zone, the frequency is also reduced due to attenuation of energy. Fig.8C is the sweetness section for the Hai Su Den basement.

3.1.8. Reflection Intensity

Reflection intensity is the average amplitude over a specified window multiplied with the sample interval. Visually, reflection intensity can help to highlight the lineament of faults and indicate zones of high fracture density (Fig.8D).

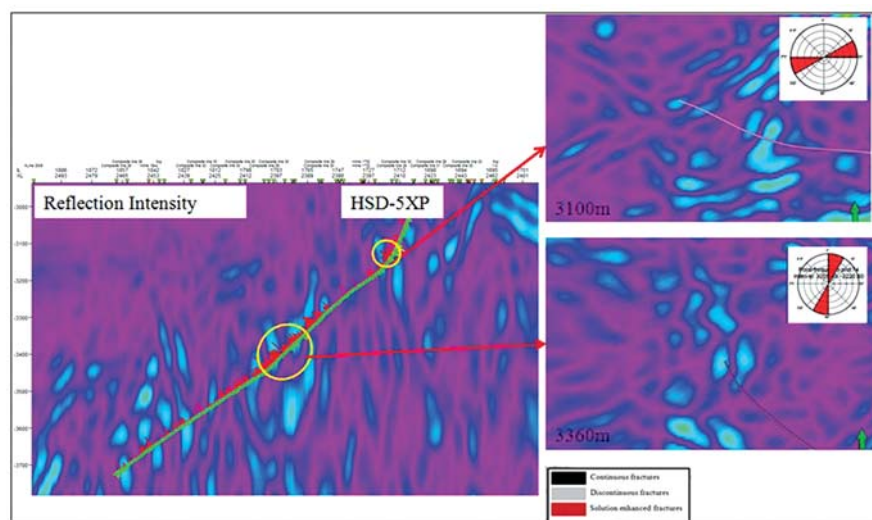


Fig.11. Comparison between reflection intensity and HSD-5XP well fracture porosity (red curve) on both section and depth slices

3.2. Quantitative analysis of the selected seismic attributes

The latest six seismic attributes and RAI were chosen for quantitative analysis to select the optimum seismic attributes for further porosity model building using ANN.

Based on the quantitative analysis, the three following seismic attributes were selected as the optimum fracture porosity attributes.

3.2.1. Sweetness

Fig.9 shows a comparison between the sweetness attribute and well fracture porosity in both

vertical section and different depth slices. It is clear to see that the seismic attribute (blue colour) is consistent with the well data not only in location of good fracture zones, but also with dip and azimuth of the fracture systems.

3.2.2. Gradient magnitude

Gradient magnitude attribute has a good tie with the well fracture porosity in location of good fracture zones and in dip and azimuth of different fracture systems (Fig.10).

3.2.3. Reflection Intensity

Similar to the Sweetness and Gradient magnitude attributes, Reflection Intensity also has a very good tie with the well data (Fig.11).

4. Porosity model building using ANN and Co-Kriging technique

4.1. ANN

ANN is applied to integrate the selected seismic attributes with well fracture porosity to predict the distribution of porosity within basement.

ANN is a tool for automatically finding the relationship between multiple known parameters and a single unknown parameter. The behaviour of a neural network is defined by the way its individual computing elements are connected and by the strength of those connections, or weights. The weights are automatically adjusted by training the network according to a specified learning rule until it properly performs a desired task.

Supervised ANN is an algorithm that takes multiple inputs and returns one or several outputs. These inputs may match with log values, seismic attributes, surface values or properties from the same cell. Each input is multiplied by a weight; the result is summed and passed through a nonlinear function to produce an output [5].

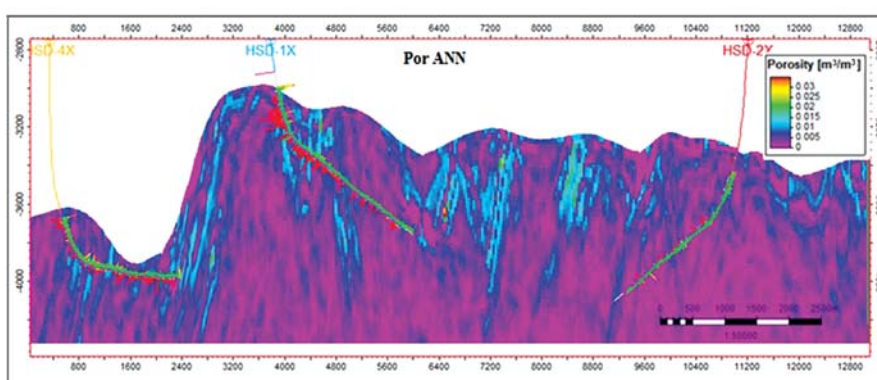


Fig.12. Vertical section of porosity model using ANN.
The red curves are well fracture porosity

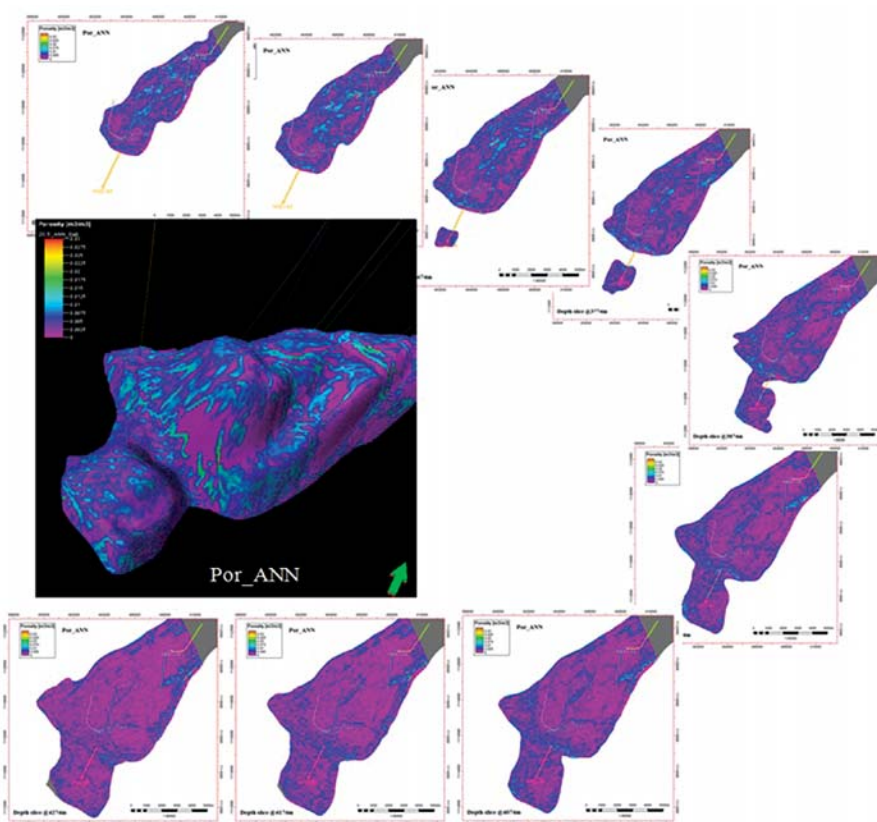


Fig.13. Porosity model and depth slices using ANN of Hai Su Den fractured basement

The set of 03 selected seismic attributes (*Reflection Intensity, Gradient Magnitude, and Sweetness*) was run in supervised mode using ANN and well fracture porosity was used as training data. We can observe that this optimum seismic attribute set has a good correlation coefficient (as 0.76) with well porosity, therefore the result of predicted porosity by ANN is highly reliable. Figs.12 and 13 show a very good consistence of well fracture porosity with the fracture porosity predicted by using ANN.

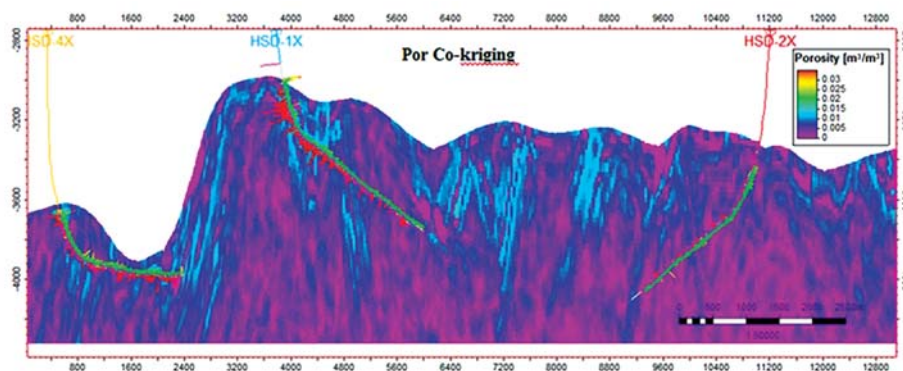


Fig.14. Vertical section of porosity model using Co-Kriging technique of Hai Su Den fractured basement

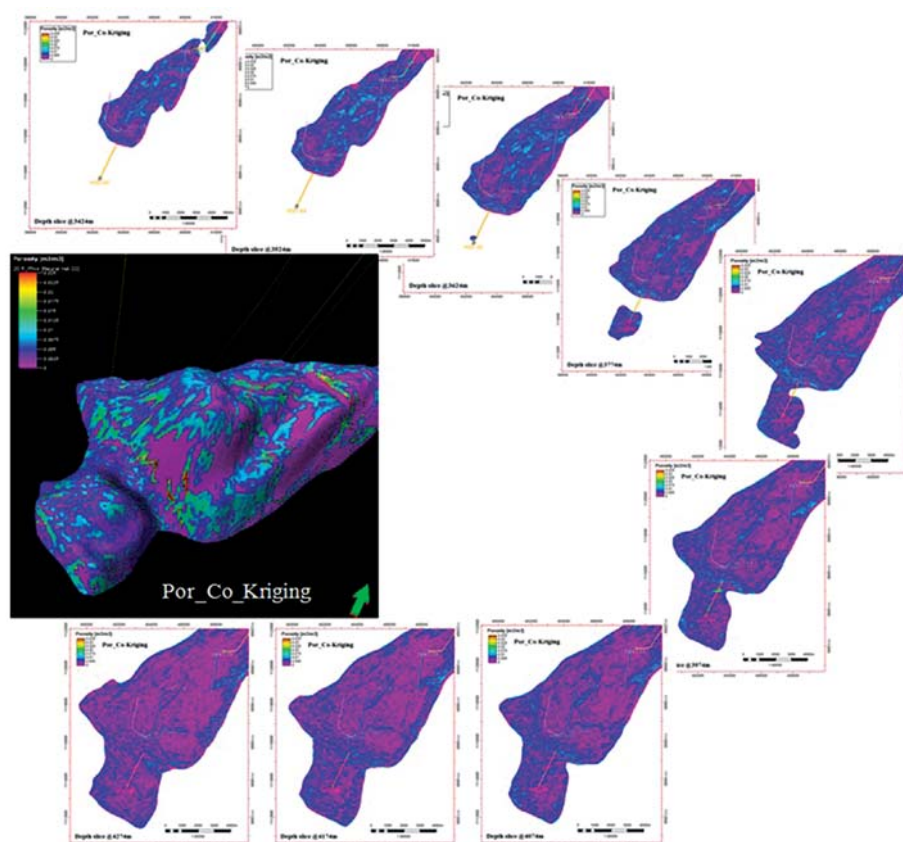


Fig.15. Porosity model and depth slices using Co-Kriging technique of Hai Su Den fractured basement

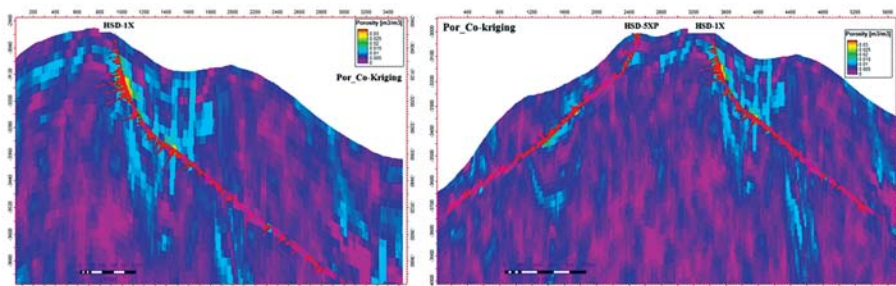


Fig.16. Comparison between secondary porosity modelling using Co-Kriging technique and well's porosity on section

4.2. Co-Kriging technique

Based on the result of predicted fracture porosity model using ANN, Co-Kriging steps have been taken to correct the trend and extent of fractures in the model by well parameters, fracture parameters and tectonic elements of the study area. In this process, the model was used as a secondary variable, while porosity data of wells was used as a primary variable. In addition, a distribution of fractures in the secondary porosity model was also governed by geo-tectonic parameters such as dip, azimuth, major and minor values of fault systems or fractured zones [5].

Co-Kriging is a method that is used for simulation of oil-field by interpolating algorithms, which based on the analysis of error changes with distances. Co-Kriging solution is used to integrate the primary variable with secondary variables by calculating correlation coefficients and the experimental variogram statistics function. Figs.14 and 15 present a very good correlation between well fracture porosity (red curves) and the fracture porosity model of the Hai Su Den basement, which was built by integrating ANN and Co-Kriging techniques.

In order to assess the reliability of the porosity model, a series of correlations were carried out. The distribution and the relationship between well fracture porosity and porosity received from ANN and Co-Kriging show a very high degree of correlation (Fig.16).

5. Conclusions

The quality of Hai Su Den 3D 2009 Beam PSDM seismic data is

good for the basement; as a result many seismic attributes could have positive results in qualitative and quantitative analysis for identification and outlining of good fracture zones inside the basement and for characterisation of the fracture systems.

The seismic attribute set which can optimise fracture porosity has been selected, consisting of the three following attributes: *Reflection Intensity, Gradient Magnitude, Sweetness*.

In the case of good seismic data as in the Hai Su Den field, integration of ANN and Co-Kriging techniques was proved as a good method to build fracture porosity model for the fractured basement reservoir.

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EVALUATION OF WATER SATURATION IN THE LOW RESISTIVITY RESERVOIR OF TE GIAC TRANG FIELD, BLOCK 16-1, CUU LONG BASIN, OFFSHORE VIETNAM

Cu Xuan Bao, Pham Thi Thuy, Bui Huu Phuoc, Nguyen Quan Phong
Hoang Long - Hoan Vu JOC's

Summary

It is well known that there is a series of oil fields in the Cuu Long basin that were discovered in low resistivity Early Miocene sequences, and the Te Giac Trang field is a case that challenges formation evaluation for water saturation of the pay sands in the reservoirs. It is believed that the low resistivity is a result of the effects of many factors such as thin beds, the low degree of sand compaction, the presence of highly conductive minerals (pyrite etc.), and montmorillonite that significantly increases the surface conductivity, sorting of the sand and type of cement.

In the Te Giac Trang field, for the water saturation calculation, an approach was used with the traditional shaly sand model and modified Archie equation constants. The said method combined with the results of pressure pretests allows us to minimise the uncertainty of the estimated water saturation for these low resistivity pay sands.

Key words: Early Miocene, low resistivity, J function, clay, thin bed, water saturation, pressure, high permeability, low permeability, Te Giac Trang field.

1. Introduction [1 - 3, 6 - 10]

The Early Miocene sequence is the second big oil zone after the basement section and oil is produced from low resistivity sandstone reservoirs of the Bach Ho formation in the Te Giac Trang, Bach Ho, Rong, and Su Tu Den fields.

The Te Giac Trang field is located in Block 16-1 of the Cuu Long basin, approximately 120km from Vung Tau city. The Hoang Long Joint Operating Company (HLJOC) is licensed to operate this block. The field targets multi-pay objectives within the primary target Early Miocene Bach Ho formation (Bl.1 sequence) sandstones and the secondary target Late Oligocene Tra Tan formation (C sequence) sandstones.

The Te Giac Trang field is divided into H-1, H-2, H-3, H-4 and H-5 by fault blocks and lies along a south-plunging regional scale anticlinal trend, crossed by E-W faults and a subordinate set of SW-NW faults.

The Early Miocene (Bl) sequence is subdivided into Late Bach Ho (Bl.2) and Early Bach Ho (Bl.1). The Late Bach Ho sediments were deposited in shallow and open marine environments. The Early Bach Ho, deposited in coastal, fluvial, deltaic and shallow marine environments, is subdivided into three units: ULBH, ILBH5.1 and ILBH5.2. Well log practice identified low resistivity contrast subsequences. Low-resistivity pay is generally characterised by pay zones that cause deep resistivity log curves to read from 0.5 to 5Ω.m. This is often attributed to a combination of shale content, mineralogy, microporosity, grain size and bed thickness.

Low-contrast pay implies a lack of resistivity contrast between pay sands and adjacent shales or wet zones. This problem is most commonly seen when the resistivity tool encounters a zone that contains fresh water (or water of low salinity). As salinity decreases, the electrical pathway through a body of water becomes weaker and more dispersed, thus causing the water to become less conductive (or conversely, more resistive). Therefore, while the resistivity of the pay zone may not be low, the resistivity of the water leg is high enough to make it difficult to distinguish between pay and wet zones. However, in the Te Giac Trang field the water salinity is very high, in this case low contrast pay implies a lack of resistivity contrast between pay sands and adjacent shales.

A number of factors have been found to act on the logging tool to produce low resistivity or low contrast pays, including the following:

- Bed thickness: some pay zones are simply too thin to be resolved by the logging tool.
- Mineralogy: conductive minerals (such as pyrite, glauconite, hematite, or graphite, smectite, illite, chlorite, kaolinite) or rock fragments can have a pronounced effect on resistivity response.
- Structural dip: dipping beds produce significant excursions on the resistivity log when orientation between the tool and the bed deviates from normal.
- Clay distribution: classified as either dispersed, structural, or laminated - all capable of holding bound water.

- Water salinity: high salinity interstitial water causes low resistivity within the pay zone, while low salinity water can cause low contrast pays.

- Grain size: very fine grain size can lead to high irreducible water saturation.

Any combination of the above: often a combination of inter-related factors causes the logging tool to read lower resistivity than normal inside a pay zone.

In the Te Giac Trang field, probably the most common cause of low resistivity pay is the simple combination of thin beds containing highly conductive shales (and their associated bound water), along with thin pay sands which are below the vertical resolution of the logging tool, as shown in Fig.1, below, of conventional core through a laminated interval in the Early Miocene sequence. It is observed that there were certain amounts of conductive mineral such as pyrite found in the core sample, which definitely play some role in the low resistivity nature of the Early Miocene reservoirs.

The presence of clay causes a conductive path due to the presence of an excess of cations clinging to negatively charged clays. The movement of cations along the surface of the clay constitutes an electrical path. The larger surface area of clays presents more Cation Exchange Capacity,

thus lowering the resistivity of the hydrocarbon sands. The Table 1 shows the abundant presence of all the clay minerals, particularly smectite that is the main cause of low resistivity in the hydrocarbon zones.

In the Early Miocene reservoirs in the Te Giac Trang field, the sandstones are thinly interbedded with the low resistivity shales. It is commonly observed that the sandstones thicknesses are less than the tool's vertical resolution. Even with thicker sand layers, the resistivity readings are normally affected by bedded claystones. As a result, the resistivity readings of the oil bearing sandstones are lower than they should be. Pyrite is a very good conductive matrix. If pyrite was present in the formation, the measured resistivity of the formation would be affected by conductive pyrite. Traces of pyrite have been observed in low Miocene sequence. This is an additional factor causing the low resistivity values in hydrocarbon zones.

All of the list above cause low resistivity contrast pay. Even if all of the above data were taken into account for saturation calculation, it would not necessarily provide more accurate estimates of water saturation due to a lot of uncertainties. The Model Saturation - Height Pc from J function is to be used in this case.

2. Using J function to calculate water saturation in Te Giac Trang field [1 - 4]

J function is a master curve that can be used to represent reservoirs of similar rock type. In the Te Giac Trang field, based on the permeability range of the test samples, there are two kinds of J functions that have been created from quality-controlled refined legacy porous plate data. Power law regressions of form were fitted to "high permeability" and "low permeability"

$$S_w = \frac{a}{J^b}$$

Table 1. The result of XRD analysis for clay fraction (< 2 microns)

MD (m)	Kaolinite (%)	Chlorite (%)	Illite (%)	Smectite (%)	Mixed layer of illite-smectite (%)
2,799.0	16.7	12.6	10.6	57.9	2.2
2,827.0	20.5	36.4	24.6	14.0	4.5
2,839.5	46.8	17.2	12.0	18.1	5.9
2,914.0	24.6	16.7	25.8	28.2	4.7
2,934.0	32.4	22.4	14.7	26.5	4.0

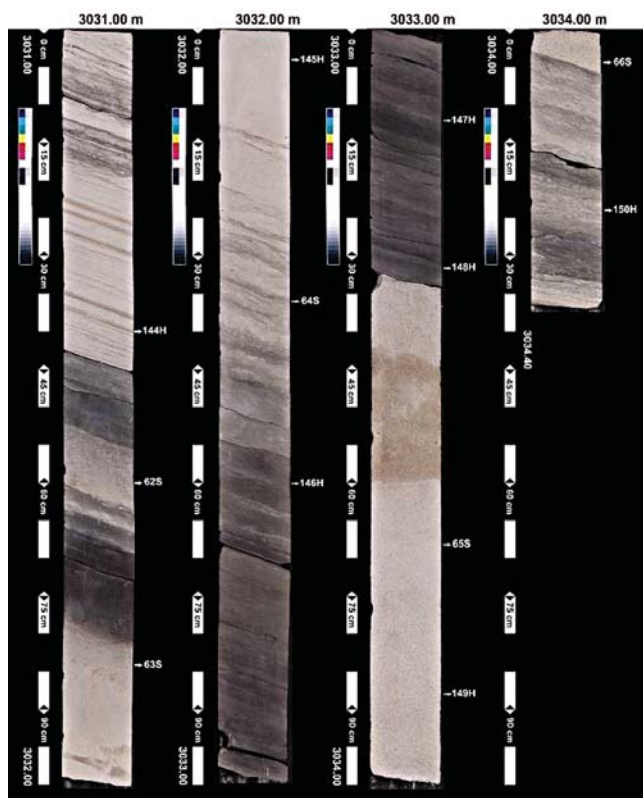


Fig.1. Core through a laminated interval in the Te Giac Trang field

Table 2. The results of XRD analysis for SWC show conductive mineral

MD (m)	Quartz (%)	K-Feldspar (%)	Plagioclase (%)	Mica and/or other clays (%)	Kaolinite and/or Chlorite (%)	Calcite (%)	Epidote (%)	Pyrite (%)	Sylvite and Halite (%)
2,839.5	49.5	16.6	14.3	5.8	11.1		1.3	1.0	0.4
3,066.5	43.3	11.2	25.8	3.2	13.6		1.3	1.0	0.4
3,116.5	28.9	11.1	17.7	15.4	24.4		1.0	0.9	0.5
3,174.5	40.8	30.1	17.2	2.1	6.6	1.5	0.7	0.9	0.3
3,181.0	43.4	23.5	21.2	2.0	7.6		1.2	0.7	0.4
3,220.0	70.2	5.9	4.3	12.4	5.0	0.6	0.6	0.6	0.6
3,297.5	43.2	15.3	19.2	2.0	17.0	0.8	1.2	0.9	0.5
3,415.0	57.8	13.5	15.2	3.4	8.3		0.7	0.6	0.5
3,425.0	60.3	13.3	15.0	2.1	7.7		0.6	0.6	0.4

Table 3. The water-mud filtrate samples analysis salinity

No	Oil gravity (°API)	Water resistivity 25°C (Ω.m)	Salinity 25°C (ppm)
1	41.7	0.1100	59,259
2	39.8	0.0779	90,269
3	39.4	0.1536	40,533
4	39.1	0.1195	54,098
5	39.9	0.0738	96,579
6	40.5	0.0871	78,748
7	35.8	0.0641	115,487

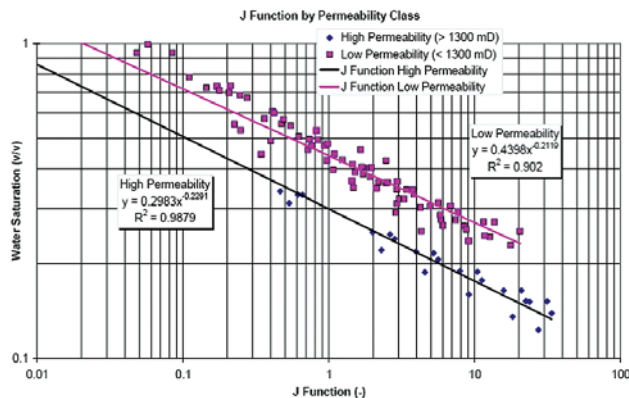


Fig.2. Relationship between J function and saturation

In Fig.2, the permeability J function extrapolation by setting $P_c = 0.01$ psi at $S_w = 100\%$.

J functions are as below:

Low Permeability (< 1,300mD)

$$S_w = \frac{0.4398}{J^{0.2119}}$$

High Permeability (> 1,300mD)

$$S_w = \frac{0.2983}{J^{0.2291}}$$

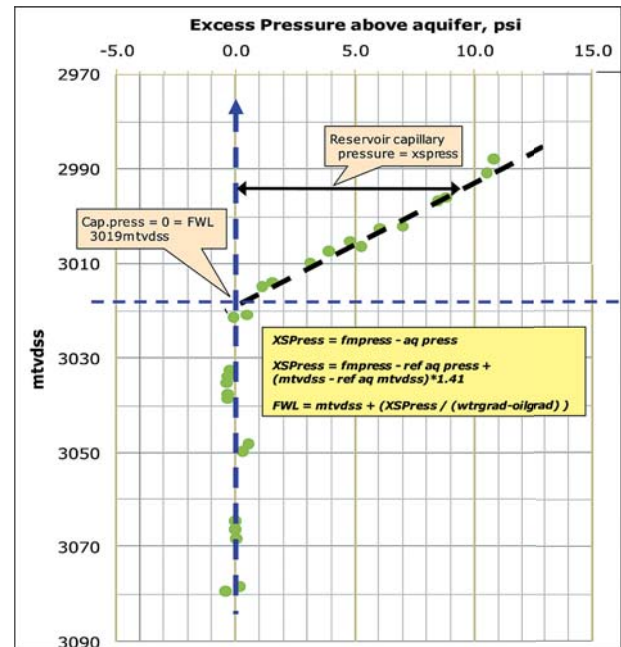


Fig.3. Excess pressure above FWL

Both of the J functions are converted to Height above the free water level as below:

$$S_w = \frac{a}{\left[\left(\frac{0.2166x(\rho_w - \rho_o) \times H}{\sigma \times \cos\theta_{res}} \right) \sqrt{\frac{K_a}{\phi}} \right]^b}$$

Where:

ρ_w : Water density gradient (0.428psi/ft),

ρ_o : Oil density gradient (0.29psi/ft),

$\sigma \times \cos\theta_{res}$: Adhesion force at reservoir conditions ($\sigma = 14 - 20$ dynes/cm, $\theta = 30^\circ$),

H: Vertical height above free water level (FWL) by excess pressure (ft),

S_w : Water saturation (%).

MICROBUBBLE DRILLING FLUID (APHRON): NEW TECHNOLOGY FOR DRILLING IN DEPLETED RESERVOIRS

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Summary

Lost circulation is a severe problem in drilling processes, especially in depleted zones. Microbubble (aphron) drilling fluid is a novel technology that possesses excellent advantages compared with other lost circulation prevention methods. The three-layer structure of microbubbles not only lessens the density of fluids, but also acts as stable bridging materials by which cracks in depleted zones could be sealed effectively. These features result in successfully reducing lost circulation. Though possessing an excellent potential for preventing lost circulation, this kind of fluid has not yet been studied in Vietnam. This paper will briefly introduce the topic of microbubble drilling fluid, including the structure and composition of aphon, how this fluid works and recent developments of this technique in drilling oil fields around the world.

Key words: Aphon, microbubble drilling fluid.

1. Introduction

Lost circulation happens due to the difference between the hydrostatic pressure of the drilling fluid and the reservoir pressure, leading to fluid penetration into cracks. In the case of operating processes, if no solution is found for this problem, drilling processes must be suspended, resulting in considerable economic damage.

An alternative, which is recently developed and is widespread, is the underbalanced drilling technique. This method, however, requires extremely expensive equipment and special protective measures. Amongst other special drilling solutions developed for operating in depleted zones, one novel drilling solution, using a particular drilling fluid, has attracted the attention of drilling specialists and companies.

The fluid, known as “aphron-based drilling fluid”, is water-based of low density and reduced cost. Aphon drilling fluid can be prepared by mixing surfactants, viscosity polymers and stabilisers to form aphon with a particular structure that can withstand high pressures without being destroyed.

An aphon was first found by Sebba in 1984 [1] and was described in more detail in his next report in 1987 [2].

2. Structure of aphon

The structure of an aphon is illustrated in Fig.1. Unlike conventional air bubbles which are covered by a single thin layer of surfactants, an aphon has a more complex structure. The air core of aphon is enveloped by a substantially stable tri-layer. This tri-layer consists of an inner surfactant film, covered by a viscous water shell, and the outer layer is a bi-layer of surfactants. This tri-layer structure could not only greatly enhance the stability of aphon, but also make aphon hydrophilic. The hydrophilic boundary of aphon makes the micro bubbles compatible with bulk water solution and lowers the attractive forces between them.

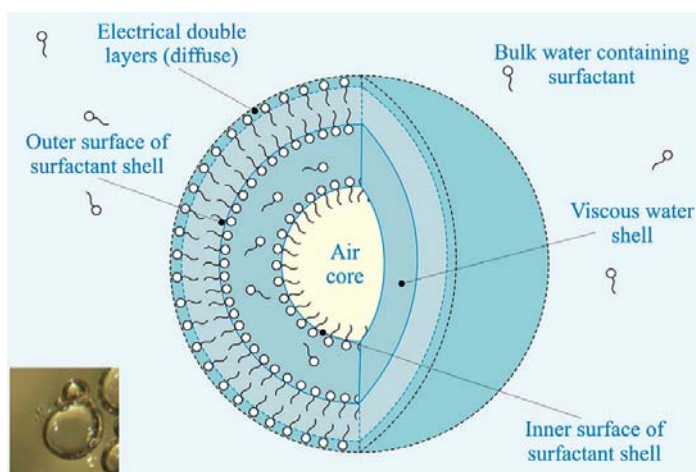


Fig.1. Structure of an aphon

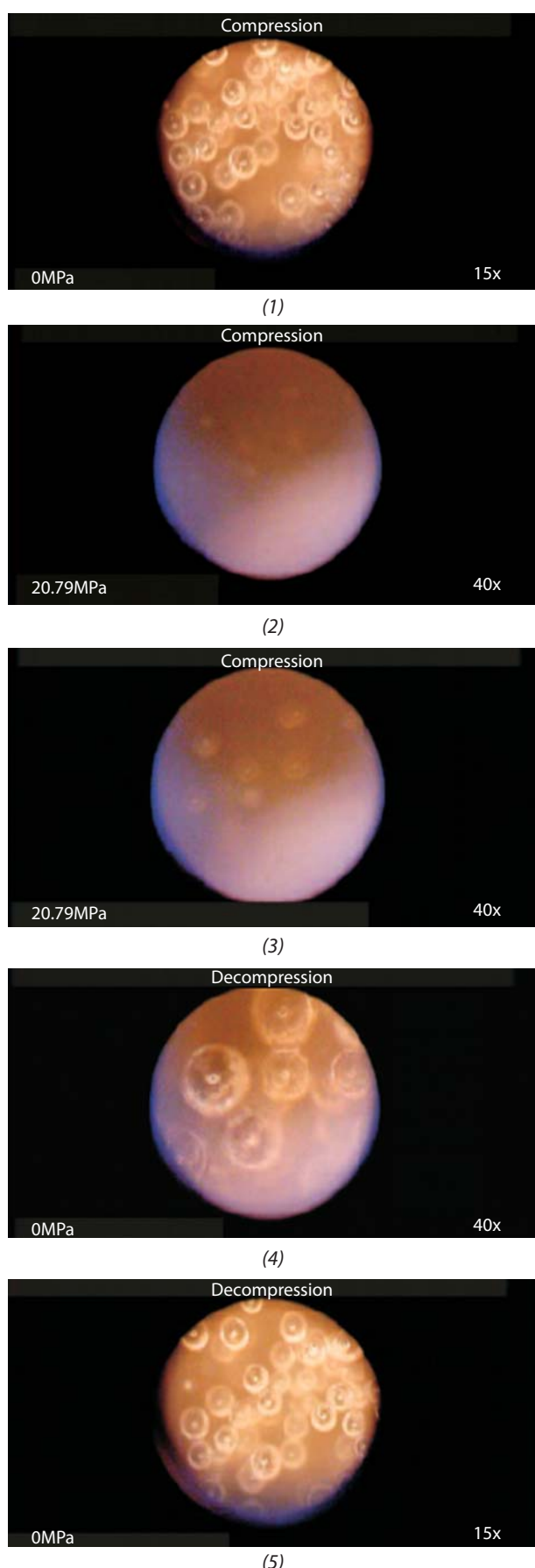


Fig.2. Surviving of aphrons at compression and decompression [7]

In contrast to conventional bubbles, which do not survive long past a few hundred psi, aphrons have been found to survive compression to at least 4,000psig (27.7MPa) for significant periods of time [3]. When a fluid containing bubbles is subjected to a sudden increase in pressure above a few hundred psi, the bubbles initially shrink in accordance with Boyle's Law. Aphrons are no exception. However, conventional bubbles begin to lose air rapidly via diffusion through the bubble membrane, and the air dissolves in the surrounding aqueous medium. Aphrons also lose air, but they do so very slowly, shrinking at a rate that depends on fluid composition, bubble size, and rate of pressurisation and depressurisation.

A very important criterion for aphron stability is shell viscosity. The middle shell must have a minimum viscosity in order to prevent the phenomenon known as the "Marangoni effect" that causes diffusion of water out of the shell into the bulk liquid [4, 5]. This thins and destabilises the shell. The rate of transfer of water is inversely proportional to shell viscosity. Therefore, addition of a viscosifier such as biopolymer is required. The viscosifier also serves to slow the flow of bulk fluid into loss zones. Because of the small amount of air incorporated in the base fluid (only 15% v/v at ambient temperature and atmospheric pressure) the density of aphron based fluid is similar to the density of the base fluid [6].

When aphron based fluid circulated through the system, rapid compression and decompression occurred. As shown in Fig.2, rapid compression of an aphron drilling fluid from 0MPa to 20.79MPa, followed by decompression back to 0 MPa, did not break the special structure of aphrons and resulted in essentially full regeneration of the aphrons. Rapid pressure cycling of aphron drilling fluids leaves most aphrons intact. Hence, the density of aphron fluids was maintained at about 0.8 to 0.9 [7].

3. Fluid invasion control

The encapsulated air within an aphron is compressed when circulated down hole. The micro-bubble volume decreases and internal pressure increases to an extent approximately proportional to the external pressure being applied. Once the drilling bit exposes a depleted formation, aphrons are brought together within the openings of low-pressure zones. There, a portion of the energy stored within each aphron is released, causing it to expand. The expansion continues until the internal and external pressures on the wall of the aphron are in balance. As the micro-bubbles are crowded into formation openings, external Laplace forces increase dramatically, causing aggregation, rather

than coalescence, of the microbubbles, resulting in a solid-free bridge without adding solid lost circulation materials [6].

The effectiveness of the seal formed by the aphrons is dependent on the size of the openings and the degree of hydrophobicity of the aphron outer shell. Small openings and strongly hydrophobic/lipophilic aphrons promote sealing. Conversely, very large openings, e.g. fractures, will generate little or no capillary pressure and, hence, no seal may be possible except at the fracture tip [6].

Aphrons bridging mechanism is illustrated in Fig.3.

4. Composition of a typical aphron drilling fluid

Components of a typical aphron drilling fluid are shown in Table 1 [7].

As presented in Table 1, water or brine incorporated with surfactants and polymers will form stabilised aphron drilling solution.

Some properties of aphron drilling fluid are described in Table 2.

5. Field experience of applying aphron drilling fluid

Brooky described the first use of aphrons in a drilling fluid application in 1998. In this case, the microbubbles were created as a minor phase in a water-based fluid. This system was used as a means of controlling lost circulation and minimising formation damage in a low pressure vugular dolomite reef zone. The microbubbles allowed the zone to be drilled to required TD, logged and drill stem-tested; this had not been possible previously [8].

This new system was applied in South America in an area where six wells were drilled using various fluids and techniques, including underbalanced drilling. Because of severe depletion, lost circulation and borehole instability, none of these wells was successfully drilled to TD. In contrast, the application of aphron technology in this field resulted in no drilling fluid losses and excellent wellbore stability even in previously troublesome shale sections. After drilling the first three wells in this field, the operator was able to eliminate the intermediate string and drill from surface casing to TD successfully [9].

Kinchen describes drilling in a highly vugular, fractured dolomite zone with good success, even

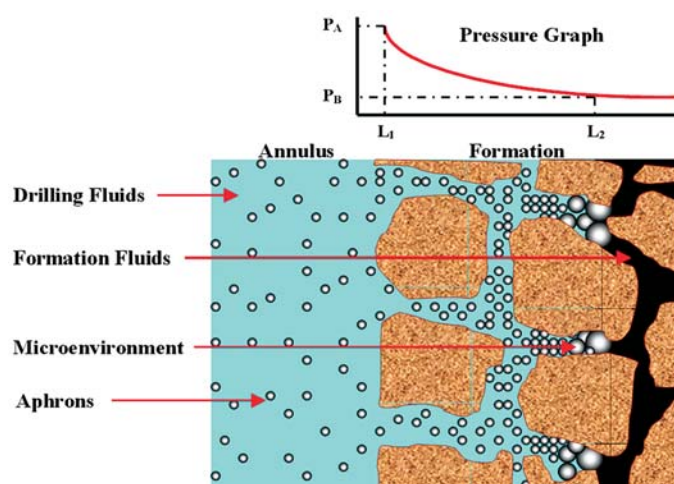


Fig.3. Aphrons bridging mechanism [3]

Table 1. Components of a typical aphron drilling fluid

Component	Function
Fresh water or brine	Continuous phase
Soda ash	Hardness buffer
Biopolymer blend	Viscosifier
Polymer blend	Filtration control agent and thermal stabiliser
pH buffer	pH control
Sufactants	Aphron generator
Biocide	Biocide

Table 2. Some properties of aphron drilling fluid [3]

Fluid properties	Unit	Expected quantity
Density	-	0.86 - 0.9
Plastic viscosity	cP	16 - 21
Yield point	lb/100ft ²	47 - 52
API Fluid loss	cc/30min	11
Low-shear-rate viscosity (0.6s ⁻¹)	cp	120,000

coring with this fluid. Besides lost circulation control, these wells came on to full production in 4 days versus 30 to 60 days average in previous wells drilled with various fluid programs [10].

Gregoire chronicles a program of drilling with an aphron drilling fluid and controlling losses in a fractured granite zone, which resulted in open-hole production almost instantaneously without treatment. Besides instant cleanup, the production rates were much higher than had been seen before with any other drilling fluid [11].

Although aphron technology has been successfully used in about 300 wells over a period of several years, it was desirable to develop a deeper understanding of the way aphron drilling fluids work and to utilise laboratory techniques for optimising field applications. A two-year research and development program was undertaken under the auspices of the U.S. Department of Energy (DOE) to obtain

laboratory evidence for the capability of aphron drilling fluids - primarily the polymer water-based system - to limit fluid invasion in permeable formations with minimal formation damage, and to provide a sound scientific basis for this behavior [12].

6. Lost circulation in Bach Ho and Rong oil fields

At depleted zones in the Bach Ho and Rong oil fields, reservoir pressure is lower than hydrostatic pressure and the reservoirs have cracks of various sizes (including macro and micro cracks). Therefore, lost circulation always happens in drilling processes with different levels at these depleted zones. According to the drilling history in the Rong oil field written by Vietsovpetro engineering for the period of ten years (1988 - 1998), there were 71 occurrences of lost circulation, with severe and complete loss accounting for 74,7%. However, until the present, there has been no effective treatment given for these problems.

The oil production has decreased in recent years, requiring drilling specialists and companies to find solutions to lost circulation problems. With the outstanding properties which have been studied and examined globally, aphron drilling fluid could be an excellent technique for depleted zones in the Bach Ho and Rong oil fields.

7. Conclusions

Aphron drilling fluids have shown the capability of effectively preventing loss of circulation in depleted zones. The applicability of this technique has been reported in seminars held by the Society of Petroleum Engineers, and it has been applied in some countries such as Yemen, Brazil and Mexico.

In Vietnam, this technique has not been studied and applied yet. Nonetheless, with excellent properties, aphron drilling fluid shows great potential for drilling at depleted zones in the Bach Ho or Rong oil fields, in which the oil production has declined sharply.

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POTENTIAL STRATIGRAPHIC PLAY IN THE WESTERN HA LONG BASIN FROM 3D SEISMIC INVERSION AND REGIONAL GEOLOGICAL CONTEXT

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Summary

There appears to be an actively working hydrocarbon system in the Western Ha Long basin (Beibuwan basin) during the Tertiary. All large conventional structures appeared leaking due to the late inversion tectonic activity. The only remain risk is the presence of a commercially sizable trap within the fetch area. With the latest 3D conventional seismic data and inversion products controlled by the information from two recent wells, a detailed litho-facial and depositional environment interpretation was carried out. The results outlined a series of areas with good reservoir potential multi-stack sand fairway surrounded and interbedded by the highly source potential lacustrine shale. These potential stratigraphic traps all have a high risk of lateral sealing. However, with the recent significant oil discoveries in similar settings and trap style in the Albert basin, East Africa, these stratigraphic plays become very attractive targets and are worthy of further studies and exploration.

Key words: Potential stratigraphic play, Western Ha Long basin.

1. Introduction

The study focused on the Western part of Ha Long basin within the geographic boundary of Block 101-100/04 of Vietnam. The basin, opened in rifting setting in early Tertiary time (Eocene - Oligocene) with a boundary faults to the North West. In late Tertiary time (Miocene to recent), the passive margin marine setting is dominant over the region. An obvious wrenching inversion has

occurred recently from late Miocene, resulting in several present day structural closures which have been the main targets for exploration drilling to date [8].

A representative section across the Eastern part of Ha Long basin (Fig.1) clearly illustrates the petroleum play concept. Oil and minor gas/condensate have been discovered and produced in this region mainly from the reservoirs of Phu Tien, Dinh Cao and Phu Cu. Main source

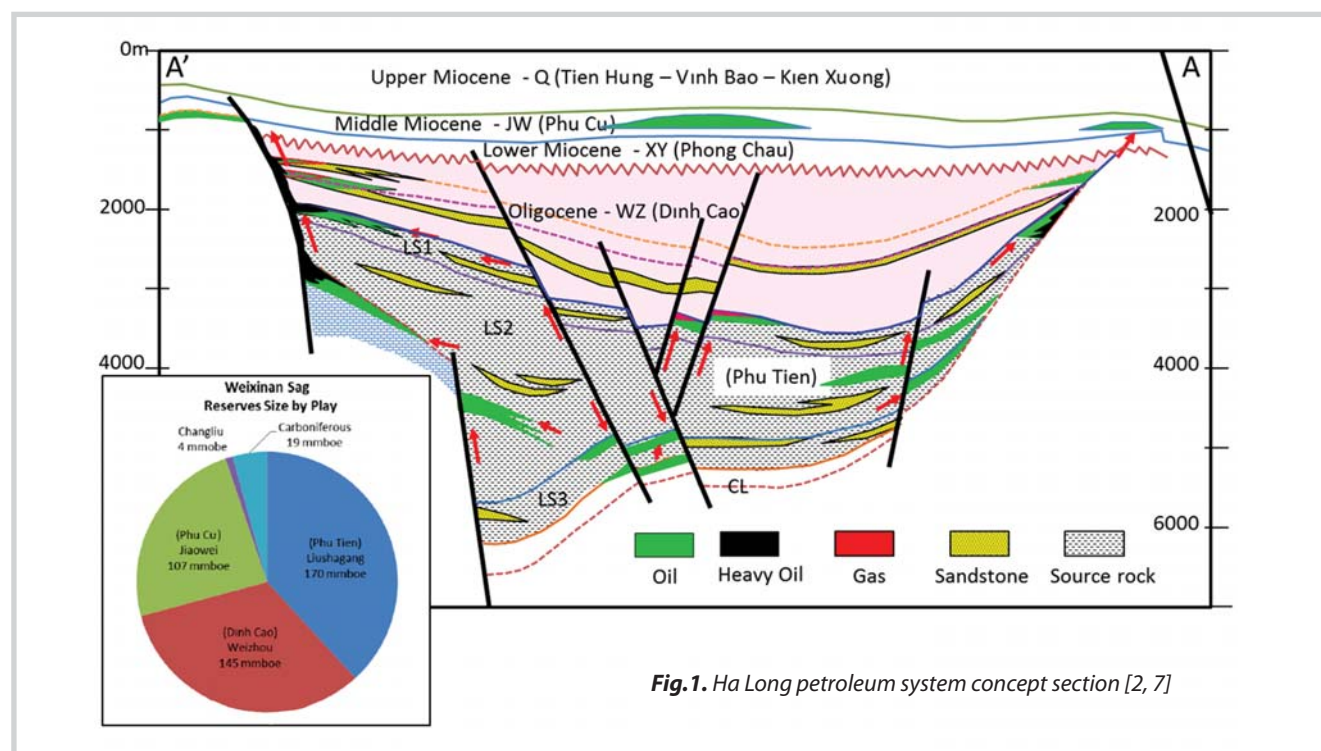


Fig.1. Ha Long petroleum system concept section [2, 7]

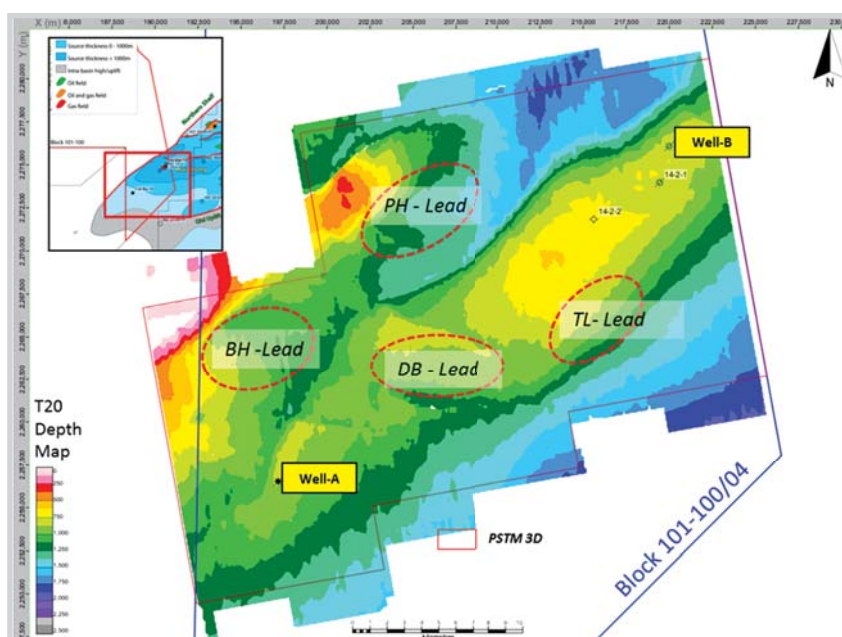


Fig.2. Database and objects

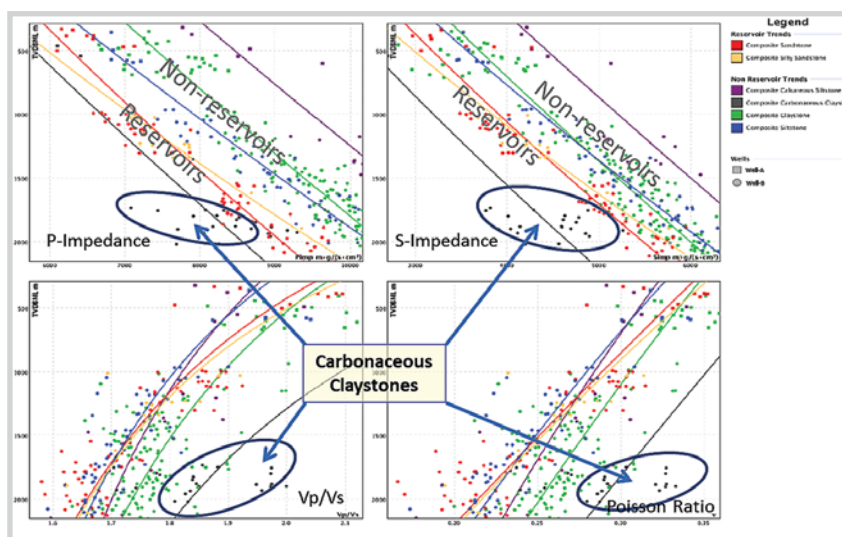


Fig.3. Well elastic properties depth trend [1]

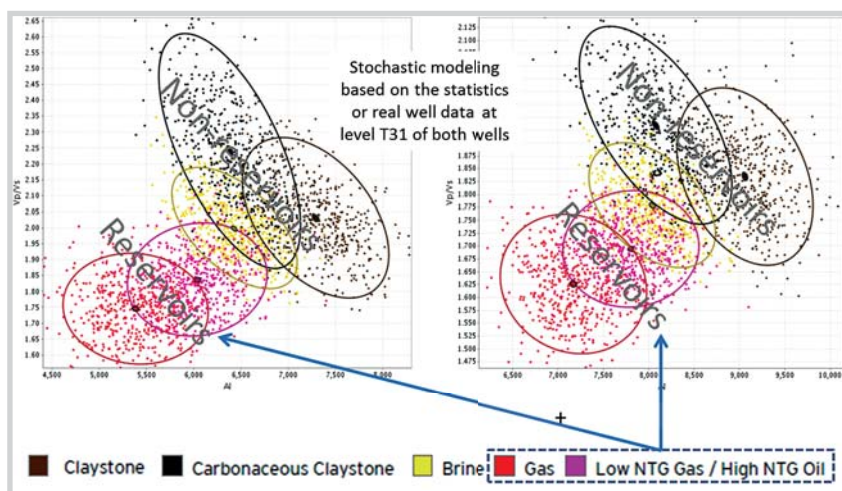


Fig.4. Stochastic well modelling [1]

rocks in the Eastern part of Ha Long basin are the Eocene lacustrine shales of Phu Tien formation. In the Eastern part of the study area, in addition to Phu Tien shales, the organic rich mudstones of Oligocene Dinh Cao formation are also considered matured source rocks since they are buried in the deeper depocenter [2].

2. Well rock physics and forward modelling

Database for the study (Fig.2) consists of 3D seismic cubes (~700km²) acquired in 2007. The seismic dataset was pre-stack time migration processed. Final full stack and partial stacks (near, mid, far) were made available. Digital wireline data from only two wells Well-A and Well-B were accessible. The whole seismic cube was then pre-stack inversion processed by DownUnder GeoSolutions in 2011 [1]. Several cubes of inversion products were then utilised for this study.

The cross-plot of elastic properties of the two wells against depth (Fig.3) shows a clear separation between reservoirs (sandstones, siltstones) and non-reservoir rocks (calcareous siltstones, siltstones and clays) on P-Impedance (AI) domain. The only exception is the carbonaceous claystones encountered at the bottom section of Well-B. These claystones appear even “softer” than the sandstones. However, they are reversely located in Vp/Vs domain that appears even higher than the other claystones and shale. Pre-stack inversion products, which utilise both AI/VpVs, are therefore, a very robust and reliable tool for lithology (in this case is reservoirs) prediction.

The follow-on stochastic AI/VpVs cross-plot (Fig.4) with the modelled fluid substitution again confirmed the good separation between reservoir and

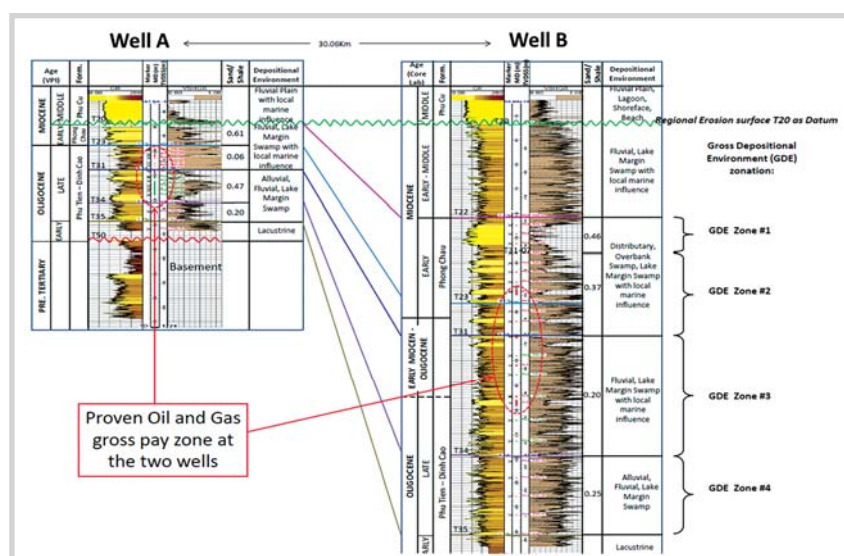


Fig.5. Well correlation and GDE definition

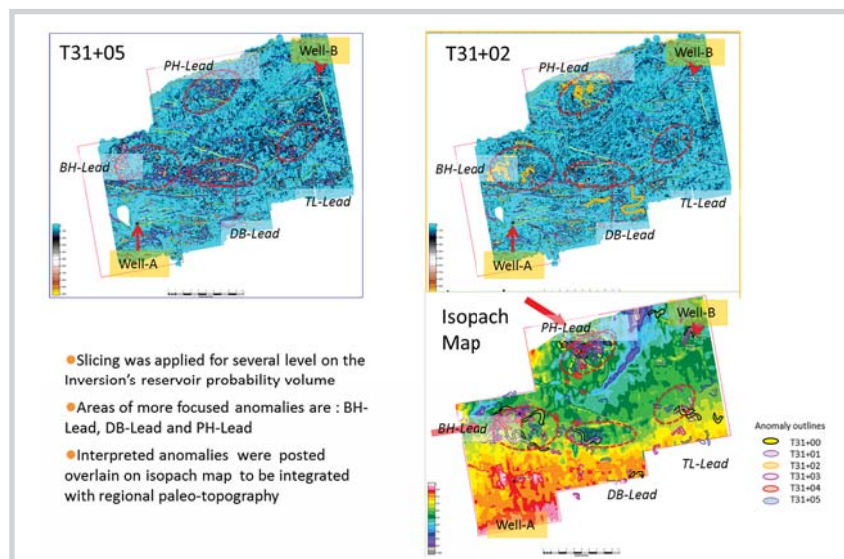


Fig.6. Slicing for inversion anomalies overlain on isopach

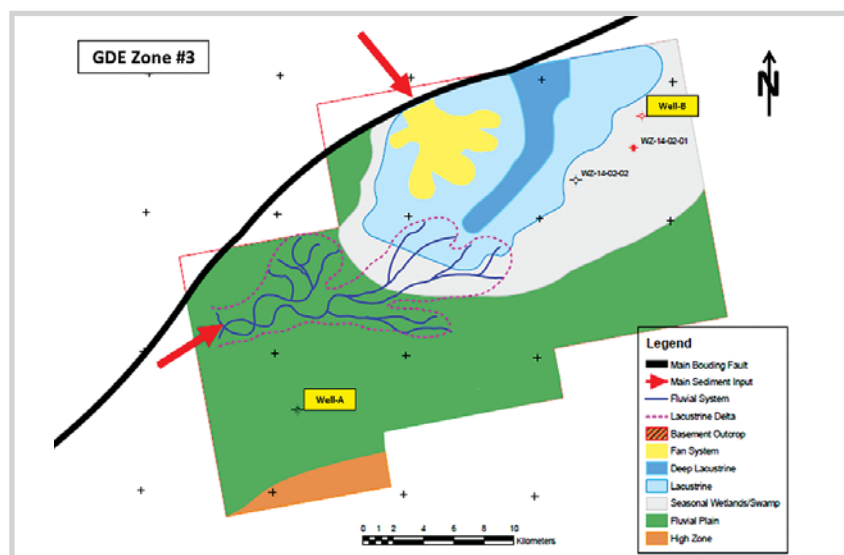


Fig.7. Gross depositional environment interpretation

non-reservoir rocks. Therefore, in actual inversion products interpretation, high net-to-gross (NTG) gas sand prediction (red) was summed with the low net-to-gross gas/high net-to-gross oil prediction (pink) to make a new cube named reservoir probability prediction. This cube is the best representation of the reservoirs' clear distinction from the other non-reservoir rocks.

It is also noted that the high net-to-gross gas is clearly delineated in the AI/VpVs domain. If good gas sand is actually present, it must be a very bright anomaly on this prediction cube. And in the pre-stack seismic domain, strong AVO class III should be obvious. The low net-to-gross gas sand/high net-to-gross oil sand is overlapped with the water wet (brine) sand. In the conventional pre-stack domain, moderate amplitude and mild difference between far and near should be expected.

3. Depositional environment and litho-facial interpretation

Depositional environment has been interpreted independently and conventionally based on regional and well data of Well-A and Well-B. Four GDE maps were produced for four stratigraphic intervals in an attempt to depict the gross depositional elements (Fig.5). Litho-facies were then interpreted on several stratal slices of the previously made reservoir prediction cube within each gross interval. The anomalies of high probability of reservoir (sand) presence were then outlined and stacked and overlain on the gross isopach map (Fig.6) for final GDE interpretation.

GDE map (Fig.7) shows two main sedimentary sources from the West and the North-Northwest and another secondary source from the East-Southeast. Due to variation of

accommodation space and the source supply, the fluvial and delta system has been shifted to back/forward to shallower/deeper locations in the lacustrine. High energy environment from the West formed good reservoirs (point bars, mouth bars, and channel sands). Good reservoirs might also exist in a fan system at the Northwest dip side. Lateral seal, there, might be good owing to smeared shale along the boundary fault.

Fig.9 shows a Southwest-Northeast cross section through Well-A, Well-B and two heavy stack anomalies areas BH-Lead and PH-Lead. Inversion reservoir prediction (upper-left) shows high probability of several stack sands deposited at BH-Lead and PH-Lead consistent with the previous litho-facial interpretation. The other section (lower-left) shows that there is low probability of good sand bearing gas presence in these two lead areas. The conventional near and far stacks (Fig.10) both show strong amplitude which highly related to the contrast between interbedded sand/shale interfaces expected at BH-Lead and DB-Lead. Far stack is just slightly stronger than the near stack. This does not support the presence of gas bearing sand. Oil sand, however, may still be present.

Fig.10 illustrates how a slice (T31+01) is tracking in section view along the inversion anomaly (reservoir probability) including the gas sand #2 encountered at Well-B. Fig.11 shows the maximum anomaly maps within the slice and its depth map. Small anomalies are observed at Well-A and Well-B which are very likely related to the gas pays founded at both wells at this level (top-right). No other

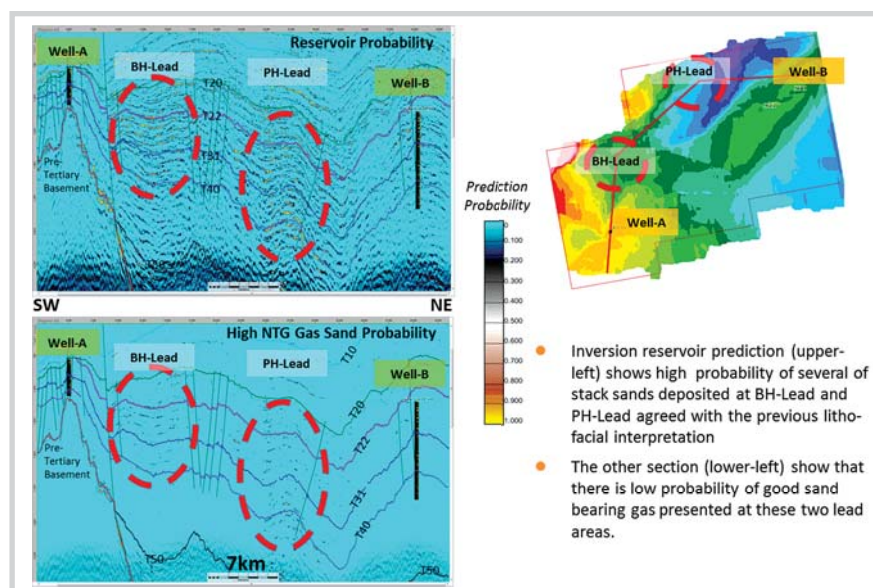


Fig.8. Inversion's prediction Southwest-Northeast cross section

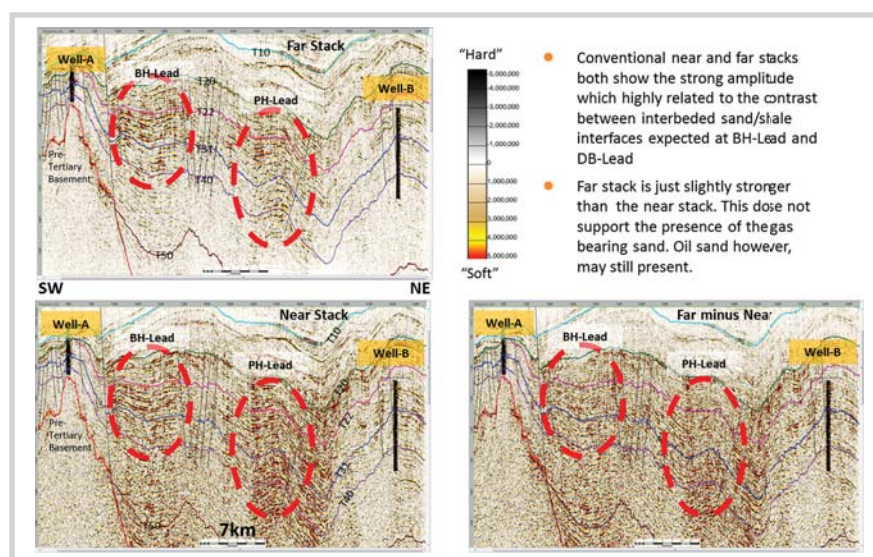


Fig.9. Conventional partial stack Southwest-Northeast cross section

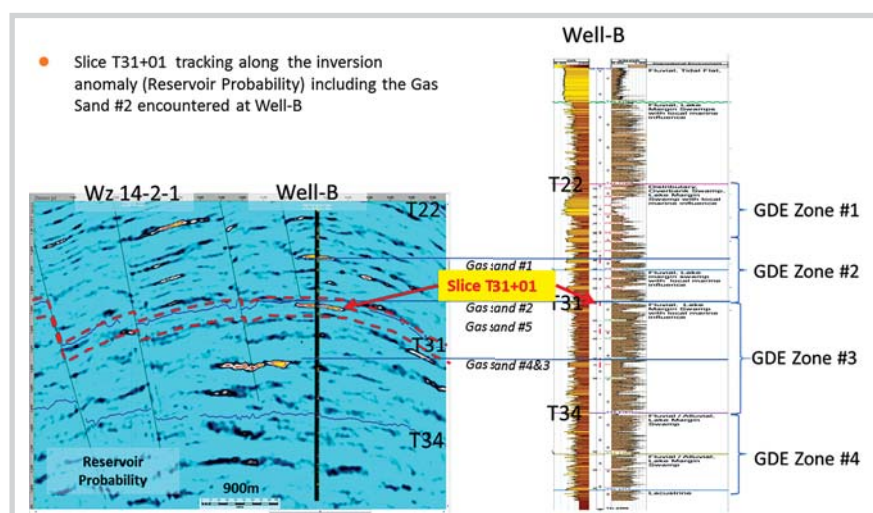


Fig.10. Inversion slice tied to well data

anomaly which may associate to high net/gross gas bearing sand on the whole 3D area was observed (top-right). The anomaly at BH-Lead and PH-Lead looks most bright (top-left), predicting a higher probability of good sand reservoir presence.

Fig.12 shows equivalent slicing of the T31+01 on the conventional partial stack data for additional interpretation. Far minus near slice (top-left) suggests more coal deposited in the South East of TL-Lead. Carbonaceous claystones are also expected down-dip of PH-Lead. The brighter anomaly on near stack (bottom-right) over the far (top-right) is also a better illustration of the above interpretation. Less coal is present at Well-B area as observed from the well data.

4. Analog geological model

An analog geological model is proposed which is the Albert lake basin at the border between Uganda and the Democratic Republic of Congo within the East African rift valley setting (Fig.13). The depositional setting is the lacustrine environment as in the Ha Long basin while the size is relatively similar. The analog proposed for PH-lead is the Kingfisher oil field (Figs.14. & 15 show the log correlation between the first two wells Kingfisher-1A and Kingfisher-2 at the pay interval. It can be obviously seen that Well-A and Well-B also show the same log motif, general net/gross ratio suggesting a similar depositional environment as those at Kingfisher wells.

5. Conclusions

Litho-facial and environment interpretations based on inversion products indicate the presence of a multi-stack good sand fairway

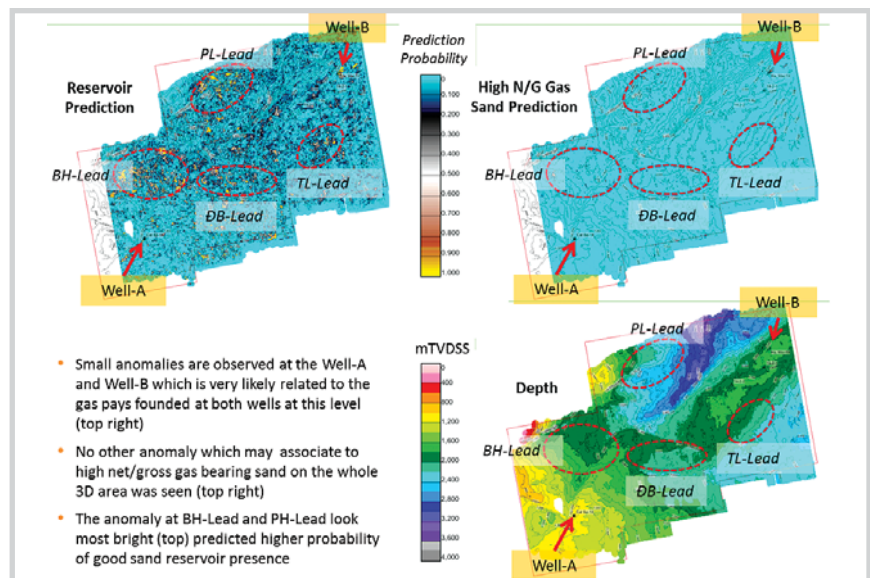


Fig.11. Inversion slice anomalies interpretation

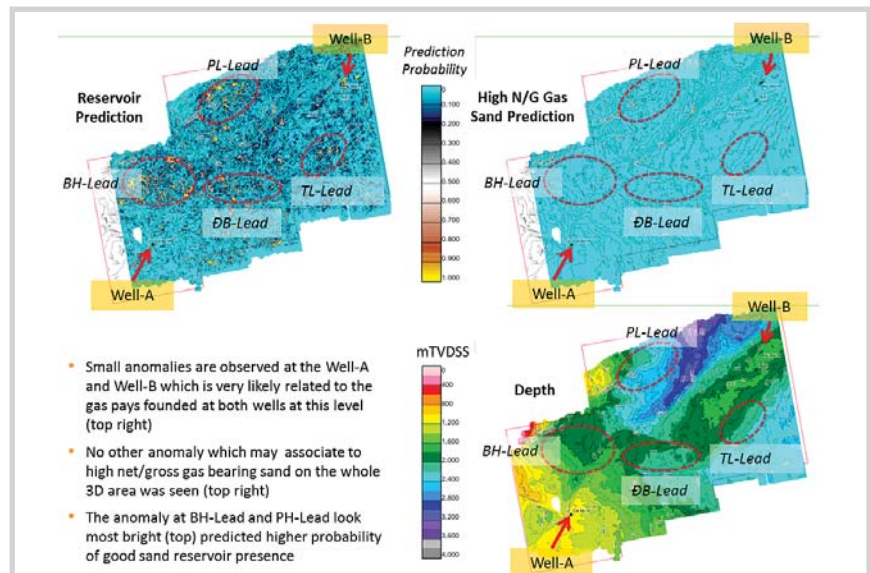


Fig.12. Partial seismic slices interpretation

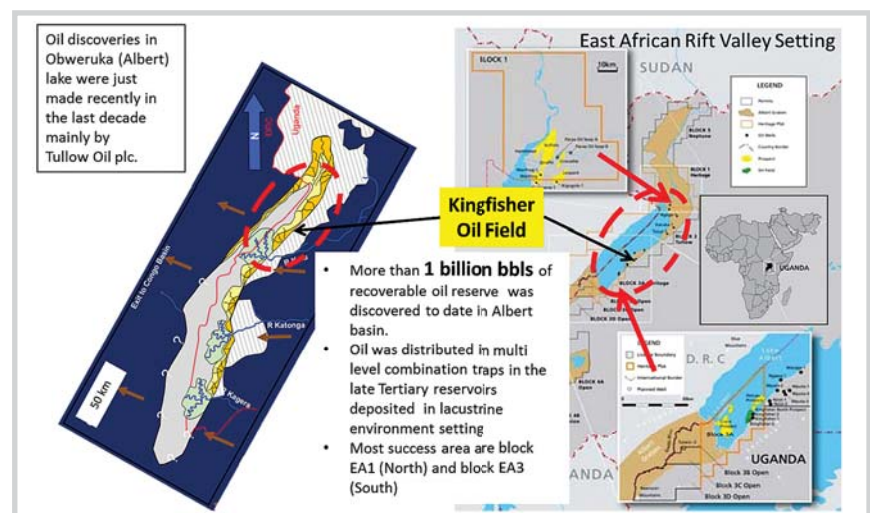


Fig.13. Analog basin - Albert lake in East Africa [4]

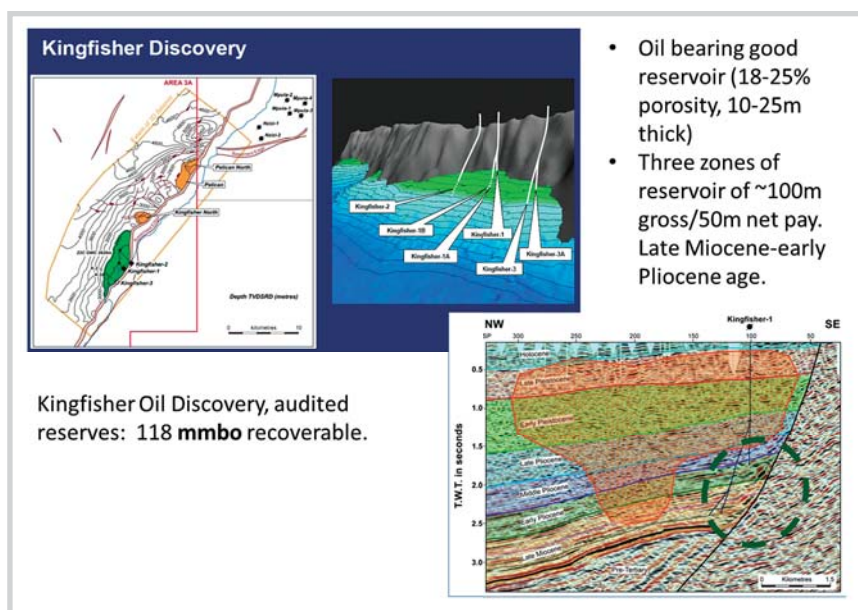


Fig.14. Analog field - Kingfisher oil field [4]

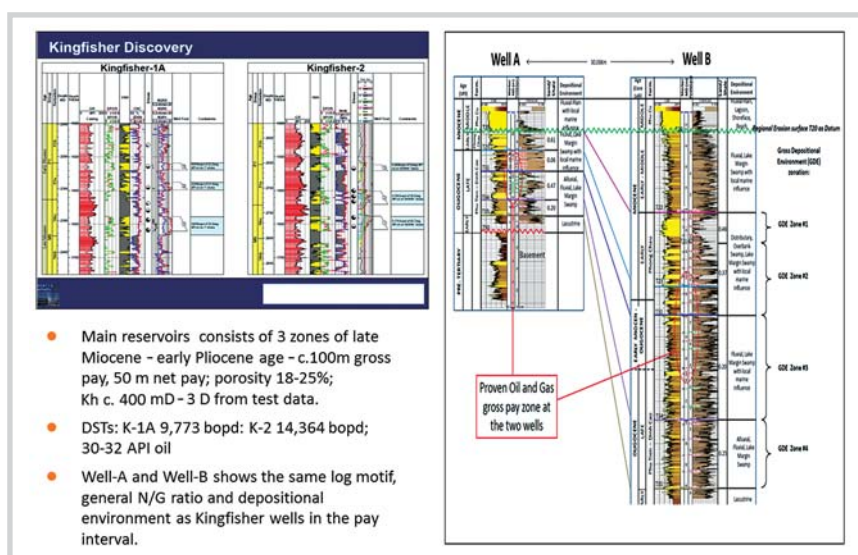


Fig.15. Kingfisher discovery - well data [4, 5]

developed and concentrated in four lead areas.

Conventional partial stack seismic also indicates that coal and carbonaceous claystones are widely deposited surrounding the PL-lead and TL-Lead.

Good sand fairway surrounded and interbedded by a lacustrine dominant carbonaceous claystones of Dinh Cao formation (already confirmed source rock potential) suggests these leads are very favoured in terms of hydrocarbon charging.

The analog from the Kingfisher oil field on similar settings in the Albert basin, East Africa supports the up-dip fault/stratigraphic sealing mechanism for this type of hydrocarbon trap.

Further fault seal analysis and updated basin modelling are recommended. However, this new stratigraphic play concept is obviously potential in the petroliferous Ha Long basin.

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TRIETHYLAMINE TEMPLATE LOCATION WITHIN CoAlPO-34 TYPE MATERIALS BY HIGH-RESOLUTION POWDER DIFFRACTION AND SINGLE-CRYSTAL DIFFRACTION TECHNIQUES

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Summary

A detailed structural study into the effects of substituted cobalt concentration within the aluminophosphate material CoAlPO-34 on the uptake of the template within the framework structure has been performed. The structure is classed as "small pore", with an aperture of ca 3.8Å, and has a structure analogous to that of the naturally occurring mineral Chabazite. Both high-resolution powder diffraction (HRPD) and single-crystal diffraction (SCD) techniques in the form of micro-crystal diffraction facilities at the Daresbury Synchrotron Source have made it possible to collect high-quality diffraction data for the range of crystalline CoAlPO-34 samples. The results showed the template location and ordering within the structure at the various substituted cobalt concentrations up to the Co:T site ratio of 1:6 expected to produce two template molecules per cage. The location of the single organic template molecule within the microporous framework is clearly shown.

Key words: Template, location, high resolution X-ray diffraction, single-crystal diffraction.

1. Introduction

Aluminophosphate framework structures analogous to the naturally occurring mineral Chabazite were first synthesised in 1984. Lok et al. of Union Carbide [1] synthesised a series of silicon-substituted aluminophosphate materials (SAPO's) and this was followed by the substitution of divalent metal ions into the AlPO framework, where the Al^{3+} is replaced by divalent Co, Mn, Zn, Mg, Fe, etc, forming MeAlPO's. These materials still command large amounts of interest today, particularly in the area of shape selective-catalysis [2, 3]. Of particular interest are the chabazitic (CHA) systems, i.e. the structure types -34, -44, and -47, differing only in chemical composition and the template species used in synthesis, and type -18 (AEI) which has a similar structure differing only in how the double six-rings stack (Fig.1). These systems are known to be effective catalysts for the conversion of methanol to light olefins, in particular being selective for ethene over higher olefins [4 - 6] which attracted considerable attention. Initially type-34 materials were prepared using tetraethylammonium hydroxide (TEAOH) as the template [1] but, since this initial synthesis several other templates have been successfully used, including morpholine [7, 8], piperidine [9] and triethylamine [10, 11]. Most of the resultant synthesis gels react under similar conditions, while some require changes in temperature, pH and time to form the specific

structure. In this study all the structures are of the AlPO-34 type synthesised using triethylamine as the structure-directing agent.

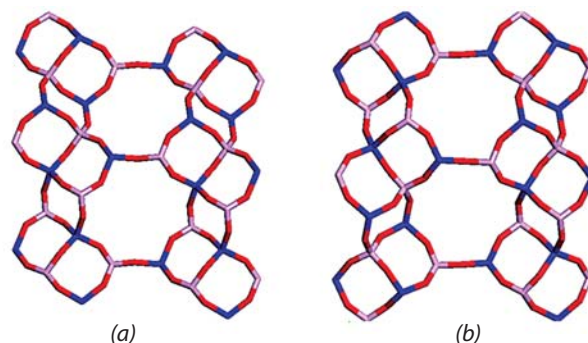


Fig.1. A section of the CHA (Chabazite) type framework is given in (a) as found in structure types -34, -44, and -47. (b) Shows the AEI structure as in type -18. The main difference is in the stacking of the double 6-rings. The Co/Al sites are shown in blue

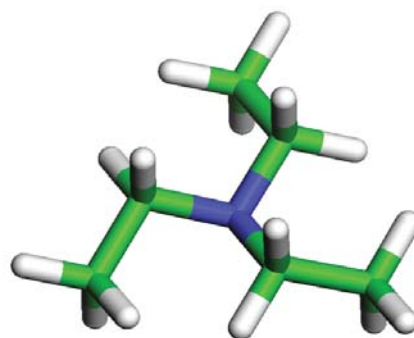


Fig.2. Structure of the template species triethylamine. The nitrogen site is shown in blue, the carbon in green and the hydrogen's are white

Uncertainty over the factors influencing the synthesis of these materials still exists; the presence or absence of a heteroatom within the synthesis gel can radically alter the structure of the resulting material. The relationship between the template and cobalt concentration is explored through the Triethylamine-templated CoAlPO-34 structure. Lewis et al [16] showed computationally that this system contains 2 template molecules per cage, but little crystallographic information has been obtained [16]. Several authors have calculated the number of template molecules located within the Chabazite-type cage of heteroatom-substituted AlPO-34 by employing single-crystal or thermogravimetric studies [14]. Usually one or two templates are found per cage; depending on which template was used and the type of heteroatom substituted into the framework, this number can vary.

Results for morpholine show that 2 templates are usually found per cage [12, 13]. However Marchese et al [13] showed that there are 1.5 molecules of morpholine per cage but also two molecules of water; this suggests that 50% of the cages might be occupied by 2 molecules of morpholine; the rest will have 1 molecule of morpholine and 4 molecules of water. If triethylamine is used as the templating agent, thermogravimetric analysis of the synthesised SAPO-34 in the presence of HF shows there are two template molecules present per cage. Computational studies [17] have shown that

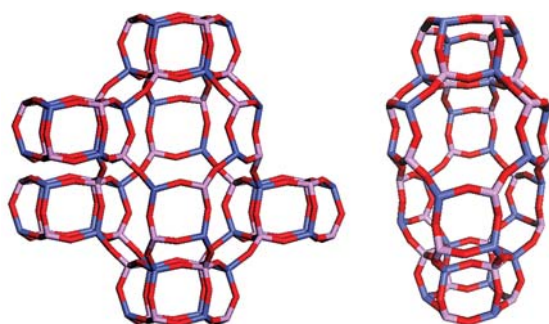


Fig.3. A model of the CHA (Chabazite) type framework. The Co/Al sites are shown in blue, the phosphorus in purple and the bridging oxygen atoms are red

Table 1. Summary of the crystal size obtained for each sample prepared. Powder samples are defined here as having a particle size smaller than $15 \times 15 \times 15 \mu\text{m}$

Co ²⁺ concentration (%) at synthesis	Powder	Single crystal
10	Yes	No
15	Yes	Yes
20	Yes	Yes
25	Yes	No

2 triethylamine molecules can fit comfortably within the cage. Synthesis of heteroatom-substituted AlPO-34 with tetraethylammonium hydroxide [2, 12, 18] and 1-propylamine [7] showed only one template molecule per chabazite cage.

Lewis et al [16] reported that, energetically, it is preferential for two template molecules to be found in each cage. The calculations show a significant increase in stability over a single template occupation. Xu et al [14] synthesised CoAPSO-34 and SAPO-34 using triethylamine in the presence of HF; thermogravimetric analysis showed the presence of two molecules per cage. Using computational techniques they also showed that two triethylamine molecules fit comfortably inside the chabazite cage. There are however, only limited single-crystal data reported for heteroatom-substituted AlPO-34 synthesised from in the absence of HF [16].

In paper we will compare the number and locations of the template molecules within the chabazite cages as a function of cobalt concentration. The CoAlPO-34 structures were synthesised with triethylamine as the structure-directing agent (Fig.2).

The structure of chabazite is comprised of double six-rings, with 3 sets of four rings attached to each six-membered ring (6-membered with respect to the number of T-atoms, a conventional notation used when describing such structures). Two of these secondary units join together to form a cage structure with intersecting 8-membered ring channels. The cage units then join together to form the 3-dimensional microporous network, (Fig.3). The 8-rings channels have a pore aperture of approximately $3.8 \times 3.8 \text{ \AA}$.

One of the problems with the detailed structural characterisation of these materials is that they rarely form large enough single crystals for study using standard laboratory single-crystal diffraction techniques. As a result of this, many of the related structures have been solved by the combination of powder diffraction and single-crystal data, as well as computer simulations in some cases [19 - 25]. However, with the advent of micro-single-crystal diffraction facilities such as Station 9.8 at the Daresbury Synchrotron Radiation Source, it is now routinely possible to collect diffraction data from crystals as small as $15 \times 15 \times 15 \mu\text{m}$. For this study, however even crystals of this size were not available for all the samples prepared, necessitating the use of both single microcrystal diffraction and high-resolution powder diffraction

techniques to identify the number of templates and their location inside the CoAlPO-34 structure. The prepared samples are summarised in Table 1.

2. Experimental

2.1. Synthesis

Samples of the CoAlPO material were synthesised hydrothermally using triethylamine as the template species. In this case a solution was first made from the

Table 2. Gel compositions (moles) used in the synthesis of CoAlPO-34 with different cobalt concentrations

Co	Al	P	H ₂ O	Template
0.10	0.90	1	60	2.0
0.15	0.85	1	60	2.0
0.20	0.80	1	60	2.0
0.25	0.75	1	60	2.0

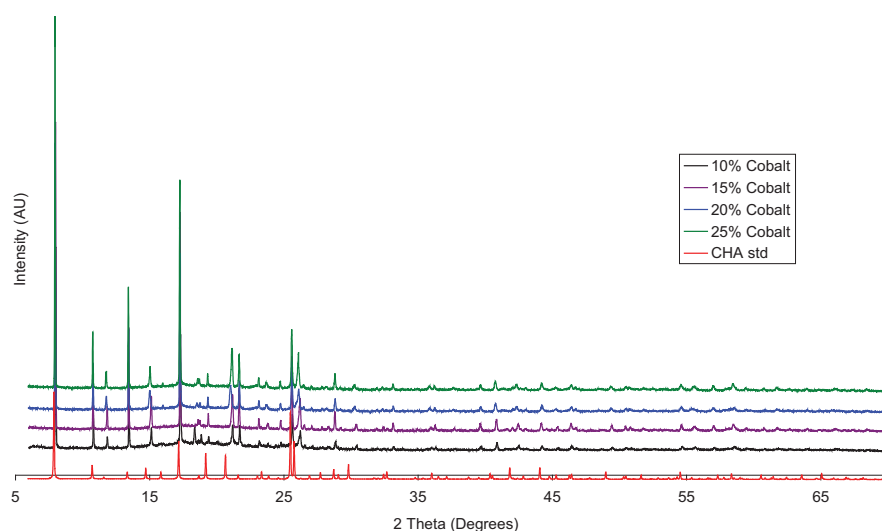


Fig.4. XRD patterns for CoAlPO-34 synthesised with differing cobalt concentrations. Intensities are arbitrary and the spectra have been offset vertically for clarity

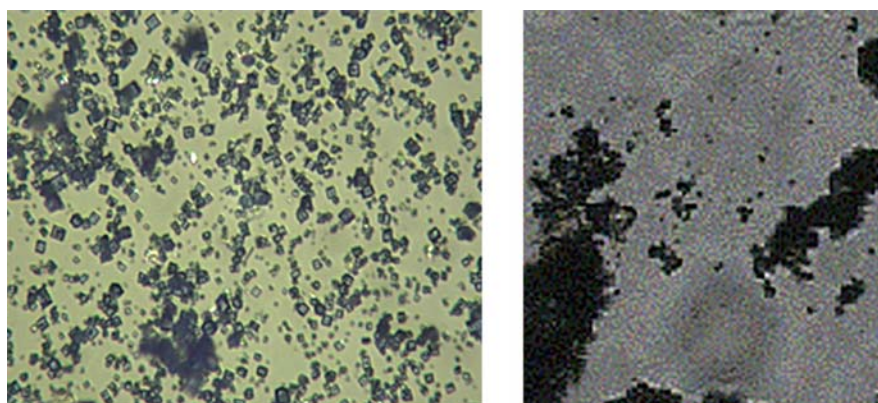


Fig.5. Optical images showing the different crystalline sizes obtained. Picture upper shows the distinct single crystals obtained for the 15% and 20% cobalt substituted CoAlPO-34 samples. Picture lower is representative of the fine powder obtained in all other concentrations for substituted cobalt CoAlPO-34 material

Co(acetate)₂ and some of the water. The aluminium source was combined with 85% phosphoric acid and the remaining water; this was thoroughly stirred before the addition of the cobalt acetate solution. The resultant gel was mixed until homogenous and the template was added at the final stage.

The gel was then mixed again until homogenous and then sealed in a PTFE liner within a stainless steel autoclave and heated under autogenous pressure at 170°C for 4 days. The product is recovered by filtration and the blue crystallites were dried at 100°C for 24 hours. The gel compositions used for the cobalt concentrations are given in Table 2. Phase purity was checked by powder diffraction recorded with a Siemens D500 diffractometer. The diffraction patterns are shown in Fig.4. All patterns are similar to that of the mineral chabazite, indicating the only phase presents being the Chabazite-related

CoAlPO-34 material. The peak positions also match those expected as in the Atlas of Zeolite Structures [26]. When studied using an optical microscope the samples split into two groups, with cubic blue crystals, where large crystals are formed, consistent with previous Chabazite-type samples. Fine powders are obtained in the second case. Optical pictures of the samples are shown in Fig.5.

2.2. Data collection

2.2.1 Single-crystal diffraction data collection

As some single crystals of the prepared material were available, single-crystal diffraction was used to locate the template molecules inside the CoAlPO-34 framework and provide supporting data to the powder analysis. Single crystal analysis of all prepared samples was not possible, as crystals of sufficient size were not always obtained. The data for the crystals were collected on Station 9.8 of Daresbury SRS using a Bruker SMART CCD area detector diffractometer equipped with

a silicon (111) crystal monochromator. A hemisphere of data was collected in each case at a temperature of 150K, employing a wavelength of 0.6892Å. The data were analysed via a least-squares refinement combined with direct methods, using the SHELXTL/SHELX-97 suite of programs [29].

2.2.2. High-resolution powder diffraction data collection

High-resolution powder diffraction data were collected on station 2.3 at the Daresbury SRS [28]. The data were collected at room temperature in capillary mode. The step size was 0.01° and the time for each step was 4s; the data were collected from 6 to 70° 2θ with a wavelength of 1.30029Å. Two patterns were collected and the data summed. The data were analysed by Rietveld profile refinement using XRS-82, the X-ray Rietveld system suite of programs [30].

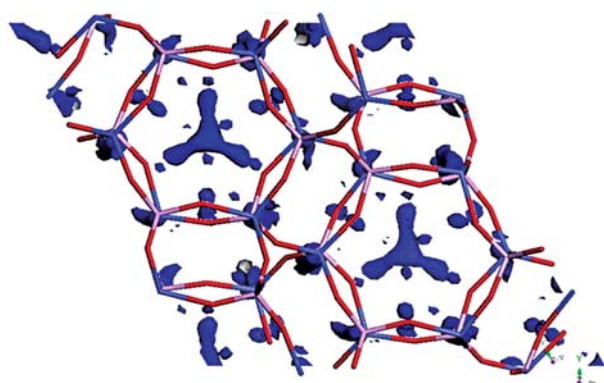


Fig.6. The observed electron density map clearly shows the template location within the cage. The framework has been overlaid for clarity and shows the Al/Co positions in blue

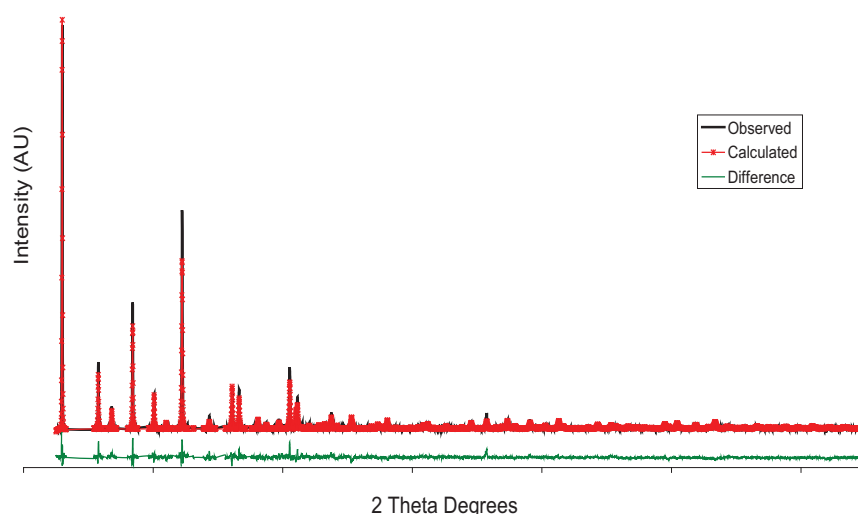


Fig.7. Best fit between calculated XRD pattern employing XRS-82 program for HRPD data of the 10% Co sample of CoAlPO-34. Collected at station 2.3, SRS, Daresbury Laboratory, using a wavelength of 1.30029Å

2.3. Data analysis

In order to maintain consistency and allowing for the fact that a single crystal is not always representative of the overall bulk sample, all the cobalt-substituted concentrations were refined using the Rietveld method, with the single-crystal studies in support. As the powder patterns obtained for each sample closely matched, each pattern was refined from the same initial starting model. This model was taken from the single-crystal data and was used to provide the atoms only for all the powder samples and also the initial cell dimensions and space group. The space group $R\bar{3}$ was used for each of the structures.

The first step for the refinement with XRS-82 is the estimation and subtraction of the background; this is done by linear interpolation between selected points before subtraction. This more effectively models the background function, particularly in this case the slight “hump” due to the amorphous scattering from the glass/quartz typically found when the samples are analysed in capillary mode. A pseudo-Voigt function was used to describe the peak shape [30]. In the initial stages, refinement of the peak shape function was performed before the inclusion of cell parameters and zero-point error. Once all these parameters had converged, the framework atomic coordinates were refined. In order to achieve a stable refinement, a few constraints were applied. In particular, the Al-O and P-O distances were restrained to 1.77Å and 1.53Å, with esd's of 0.02 and 0.01 respectively. The former distance is longer than the standard Al-O bond distance to take into account the cobalt substitution on the aluminium sites. Associated with this were some bond angle restraints, i.e. the O-P-O

and O-Al-O angles were restrained to 109° (esd 0.80) and the Al-O-P restrained to 145° (esd 8.0). After successfully refining the framework, a 3-dimensional electron density map was generated to reveal the location of the template molecules within the structure. With the template species now included within the model, again with restraints, (distances N-C 1.48Å, esd 0.01, and C-C 1.54Å, esd 0.01. Angles C-N-C 110°, esd 1.0. and N-C-C 109°, esd 1.0.), further refinement was performed to accurately determine the template location. The hydrogen atoms on the template were geometrically placed.

In the final cycles of refinement a further electron density map was generated to check for any density unaccounted for within the structure. At this point it also becomes possible to remove the framework bond restraints; all atomic and displacement parameters were then refined to convergence. The initial cell and space

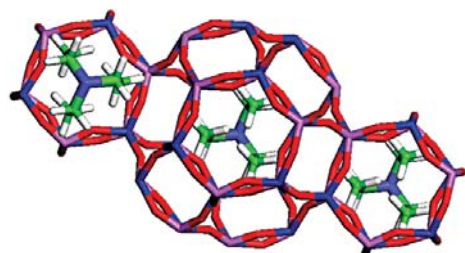


Fig.8. View of the 10% CoAlPO-34 structure, showing the position and orientation of the template within the cage structure. Al/Co sites are shown in blue

Table 3. Atom x, y, z coordinates and isotropic thermal parameters for the as prepared 10% CoAlPO-34. The cobalt occupancy here refines to 8.9%

Atom	x	y	z	Occupancy	U _{iso}
P1	0.44153	0.33860	0.22688	1.00000	1.40665
Al1	0.67258	0.56636	0.23528	0.91000	2.88348
Co1	0.67258	0.56636	0.23528	0.08900	2.88348
O1	0.54232	0.45136	0.20221	1.00000	4.97041
O2	0.34700	0.31442	0.16321	1.00000	4.97041
O3	0.46982	0.24673	0.21967	1.00000	4.97041
O4	0.40550	0.33933	0.32213	1.00000	4.97041
N1	0.66667	0.44467	0.74130	0.33333	3.79955
C2	0.69171	0.46220	0.63769	1.00000	3.79955

Table 4. Selected bond lengths and angles for the as-synthesised 10% CoAlPO-34 framework material

Atom Pair	Bond Length (Å)	Bond Angle	Degrees
P1 - O1	1.53	O1 - P1 - O2	108.8
P1 - O2	1.51	O1 - P1 - O3	110.7
P1 - O3	1.51	O1 - P1 - O4	110.8
P1 - O4	1.50	O2 - P1 - O3	109.2
		O2 - P1 - O4	109.7
		O3 - P1 - O4	107.4
Al1 - O1	1.78	O1 - Al1 - O2*A	108.7
Al1 - O2*A	1.73	O1 - Al1 - O3*A	108.5
Al1 - O3*A	1.77	O1 - Al1 - O4*A	111.9
Al1 - O4*A	1.69	O2*A - Al1 - O3*A	110.7
		O2*A - Al1 - O4*A	108.2
		O3*A - Al1 - O4*A	108.6
		P1 - O1 - Al1	147.9
		P1 - O2 - Al1*A	153.3
		P1 - O3 - Al1*B	150.3
		P1 - O4 - Al1*C	144.1
N1 - C1	1.51	C1 - N1 - C1*A	113.1
C1 - C2	1.55	N1 - C1 - C2	112.0

group information and the starting coordinates for the framework atoms were provided by the high quality single-crystal data collected for the 15% cobalt-substituted CoAlPO-34 material. The framework coordinates were directly transferred to the Rietveld refinement for the 15% cobalt-substituted CoAlPO-34 HRPD data. This structure model was refined to completion and the final framework atom positions were then used as the starting model for the subsequent powder refinements for all other substituted cobalt concentrations.

3. Results and discussion

3.1. High-resolution powder diffraction study of 10% cobalt in CoAlPO-34

The structure was refined from a starting model as described above using XRS-82, in the space group $R\bar{3}$.

The final refined unit cell parameters were $a = 13.857\text{Å}$ and $c = 14.872\text{Å}$. The final model was refined to convergence, producing final agreement factors (esd's) given in Table 3. The observed, calculated and difference profiles are shown in Fig.7. The generated difference Fourier map (difference electron density map generated to help locate the template species) was generated after the framework atom positions and displacement parameters were refined. The generated 3-dimensional map clearly identifies the positions of the template carbon atoms in the chabazitic cage, and suggests only one template per cage (Fig.6). The coordinates for the carbon atoms were then added to the model and their locations refined to convergence. With the template molecule accurately located, the model was refined to convergence with the hydrogen atoms being placed last, geometrically. The final bond distances and angles are all chemically reasonable, with the final wR_p closely matching the expected value. The final R factors are shown in Table 3 and the final difference X-ray profile is shown in Fig.6.

With the structure being refined in the space group $R\bar{3}$ there are only 2 T atom positions, and as such it is not

Table 5. Final agreement factors for the 15% cobalt-substituted CoAlPO-34 material

R Factor	Value
Profile, (R_p)	0.242
Profile, Weighted, (wR_p)	0.144
Profile, Statistically Expected, (R_e)	0.135

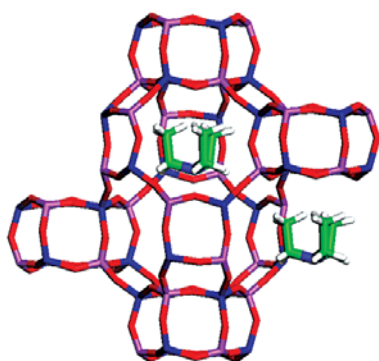


Fig.9. View of the 10% CoAlPO-34 structure showing the position of the single triethylamine template molecule. The Al/Co sites are shown in blue

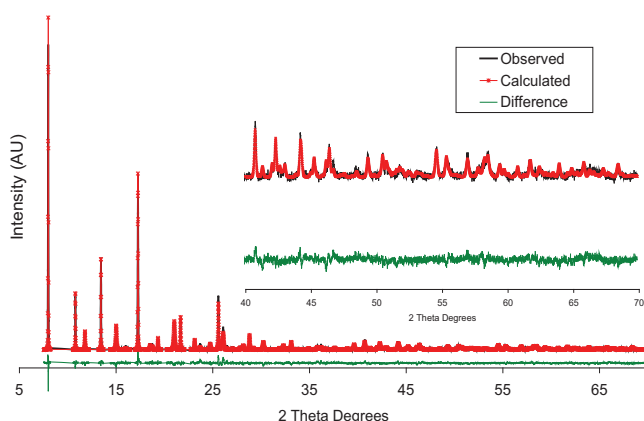


Fig.10. HRPD data for the 15% Co sample of CoAlPO-34, showing the best fit between calculated XRD pattern and observed data, employing XRS-82 program. Collected at station 2.3, SRS, Daresbury Laboratory using a wavelength of 1.30029Å

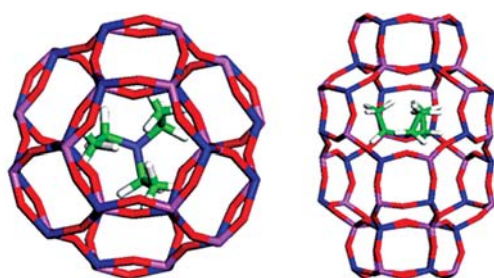


Fig.11. View of the 15% CoAlPO-34 structure, showing the position of the single triethylamine template molecule. The Al/Co sites are shown in blue

possible to assign separate positions to the Al and Co ions; therefore the Al site was refined with a partial occupancy of Al and Co (with $(Al + Co) = 1$). The cobalt content was refined and the final value matched closely the amount incorporated in the initial synthesis gel. The atomic coordinates and bond lengths and angles are given in Tables 3 and 4 respectively. The final structure derived from the Rietveld analysis clearly shows the presence of a highly ordered single template molecule contained within the cage of the framework. The atom coordinates and selected bond lengths are shown in Tables 4 and 5 respectively.

3.2. High-resolution powder diffraction study of 15% cobalt in CoAlPO-34

The initial cell dimensions were again refined along with the zero-point correction before refining the structural model. The final framework atomic coordinates from the 10% CoAlPO-34 refinement provided the starting point and this model was then refined in the same manner as the 10% data, in the space group $R\bar{3}$, with the template molecule located by the difference electron density map generated once the framework atoms had stabilised. The fully refined and converged Rietveld difference patterns are shown in Fig.10. The final refined unit cell parameters were, $a = 13.832\text{\AA}$ $c = 14.921\text{\AA}$. The cobalt content cobalt refined to 16.6%. The template was easily located from the generated 3-dimensional density map, and again shows a single template molecule occluded within the chabazitic cage (Fig.11). Again a good correlation between the final wR_p and the expected value was obtained and the bond distances and angles are all acceptable and chemically reasonable. Final agreement factors are shown in Table 5. The atom coordinates and selected bond lengths and angles are shown in Tables 6 and 7 respectively.

3.3. High-resolution powder diffraction study of 20% Cobalt in CoAlPO-34

The refinement followed the previously established route in the space group $R\bar{3}$. The refined cell parameters obtained for the 20% CoAlPO-34 material are $a = 13.831\text{\AA}$, and $c = 14.933\text{\AA}$. The difference profile is shown in Fig.12 and the final agreement R-factors are given in Table 8.

The structural model obtained is shown in Fig.13. Again we find evidence for only a single triethylamine template molecule within the structural chabazitic cage. The atomic coordinates and selected bond distances and angles are given in Tables 9 and 10 respectively.

Table 6. Atom x, y, z coordinates and isotropic displacement parameters for the as prepared 15% CoAlPO-34. The cobalt occupancy here refines to 16.6%

Atom	x	y	z	Occupancy	U _{iso}
P1	0.44351	0.33840	0.22358	1.00000	1.29710
Al1	0.67072	0.56249	0.23301	0.83300	1.04874
Co1	0.67072	0.56249	0.23301	0.16600	1.04874
O1	0.54138	0.45126	0.19611	1.00000	2.24358
O2	0.34605	0.31291	0.16285	1.00000	2.24358
O3	0.47424	0.24780	0.21279	1.00000	2.24358
O4	0.41138	0.33711	0.32124	1.00000	2.24358
N1	0.66670	0.33330	0.73384	0.33333	3.79955
C1	0.68452	0.24229	0.76079	1.00000	3.79955
C2	0.70463	0.19545	0.67334	1.00000	3.79955

Table 7. Selected bond lengths and angles for the as-synthesised 15% CoAlPO-34 framework material

Atom Pair	Bond Length (Å)	Bond Angle	Degrees
P1 - O1	1.52	O1 - P1 - O2	107.9
P1 - O2	1.51	O1 - P1 - O3	110.1
P1 - O3	1.52	O1 - P1 - O4	111.9
P1 - O4	1.52	O2 - P1 - O3	109.1
		O2 - P1 - O4	110.5
		O3 - P1 - O4	106.9
Al1 - O1	1.77	O1 - Al1 - O2*A	107.8
Al1 - O2*A	1.73	O1 - Al1 - O3*A	107.9
Al1 - O3*A	1.76	O1 - Al1 - O4*A	112.8
Al1 - O4*A	1.73	O2*A - Al1 - O3*A	109.4
		O2*A - Al1 - O4*A	109.1
		O3*A - Al1 - O4*A	109.5
		P1 - O1 - Al1	143.3
		P1 - O2 - Al1*A	153.8
		P1 - O3 - Al1*B	147.1
		P1 - O4 - Al1*C	149.4
N1 - C1	1.46	C1 - N1 - C1*A	112.7
C1 - C2	1.54	N1 - C1 - C2	105.8

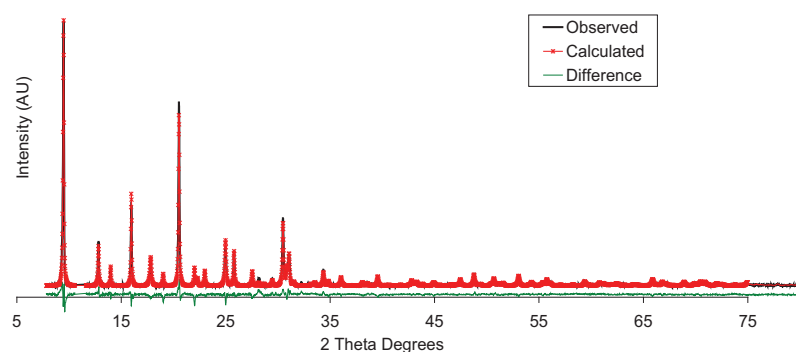


Fig.12. HRPD data for the 20% CoAlPO-34 sample, showing the best fit between calculated XRD pattern and observed data, employing XRS-82 program. Collected at station 2.3, SRS, Daresbury Laboratory using a wavelength of 1.300291Å

Table 8. Final agreement factors for the 15% cobalt-substituted CoAlPO-34 material

R Factor	Value
Profile, (R _p)	0.259
Profile, Weighted, (wR _p)	0.141
Profile, Statistically Expected, (R _e)	0.156

3.4. High-resolution powder diffraction study of 25% cobalt in CoAlPO-34

The atomic coordinates and selected bond angles and distances are given in Tables 12 and 13 respectively and are all chemically reasonable and what we would expect. The final structural model obtained is shown in Fig.15 and clearly shows the location of the single template molecule within the cage structure.

With all the structures solved and refined in the space group $R\bar{3}$, the inclusion of the centre of inversion at the centre of the chabazite cage places a symmetry-equivalent triethylamine template molecule on either side of this in order to conform to the overall symmetry of the system. However this places the two equivalent, adjacent molecules very close together, resulting in N... N separation distances shorter than an actual bond length rather than the separation of 2 adjacent groups. The separation distances are shown in Figs.16 and 17.

By lowering the symmetry for the refinement from $R\bar{3}$ to $R3$ we will remove the inversion point, and therefore subsequent data analysis in this revised symmetry should eliminate the second equivalent template molecule. To achieve this we went back to the two initial single crystal-studies at 15% and 20% substituted CoAlPO-34. These along side a representative powder data set, were re-analysed in the lower symmetry space group $R3$.

3.5. Single-crystal study of CoAlPO-34 material

Single-crystal data were collected on station 9.8 at the Daresbury SRS as described earlier and solved by direct

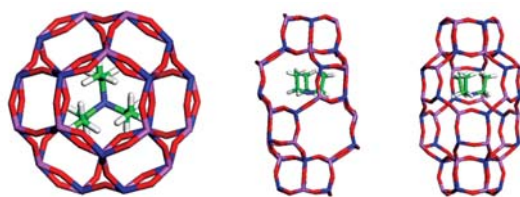


Fig. 13. View of the 20% CoAlPO-34 structure, showing the position of the single Triethylamine template molecule. The Al/Co sites are shown in blue

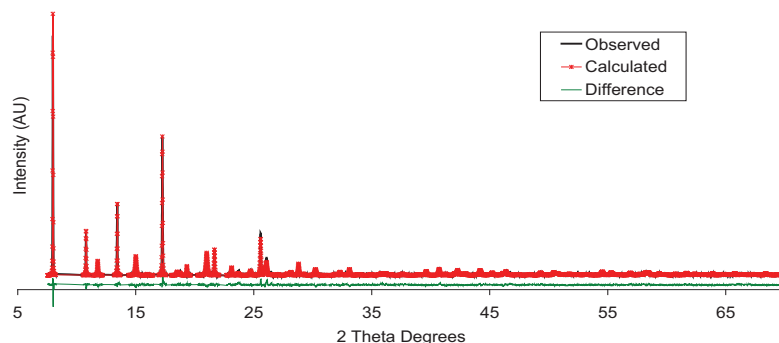


Fig. 14. HRPD data for the 25% CoAlPO-34 sample, showing the best fit between calculated XRD pattern and observed data

Table 9. Atom x, y, z coordinates and isotropic displacement parameters for the as prepared 20% CoAlPO-34. The cobalt occupancy here refines to 19.62%

Atom	x	y	z	Occupancy	U _{iso}
P1	0.44330	0.33859	0.22378	1.00000	1.57755
Al1	0.67001	0.56222	0.23280	0.80380	1.34932
Co1	0.67001	0.56222	0.23280	0.19620	1.34932
O1	0.54033	0.45148	0.19728	1.00000	2.53303
O2	0.34597	0.31343	0.16327	1.00000	2.53303
O3	0.47510	0.24873	0.21229	1.00000	2.53303
O4	0.41015	0.33693	0.32110	1.00000	2.53303
N1	0.66670	0.33330	0.73380	0.33333	3.79955
C1	0.68160	0.23970	0.76020	1.00000	3.79955
C2	0.69550	0.19050	0.67180	1.00000	3.79955

Table 10. Selected bond lengths and angles for the as-synthesised 20% CoAlPO-34 framework material

Atom Pair	Bond Length (Å)	Bond Angle	Degrees
P1 - O1	1.52	O1 - P1 - O2	107.9
P1 - O2	1.51	O1 - P1 - O3	109.9
P1 - O3	1.52	O1 - P1 - O4	111.7
P1 - O4	1.52	O2 - P1 - O3	109.4
		O2 - P1 - O4	109.8
		O3 - P1 - O4	107.7
Al1 - O1	1.76	O1 - Al1 - O2*A	107.9
Al1 - O2*A	1.73	O1 - Al1 - O3*A	108.2
Al1 - O3*A	1.78	O1 - Al1 - O4*A	112.6
Al1 - O4*A	1.74	O2*A - Al1 - O3*A	109.6
		O2*A - Al1 - O4*A	108.6
		O3*A - Al1 - O4*A	109.7
		P1 - O1 - Al1	143.9
		P1 - O2 - Al1*A	153.6
		P1 - O3 - Al1*B	146.2
		P1 - O4 - Al1*C	148.4
N1 - C1	1.45	C1 - N1 - C1*A	112.5
C1 - C2	1.53	N1 - C1 - C2	105.5

methods with the SHELX suite of programs [29]. With the structure being refined in the space group R3, there are 4 T atom positions. Discrete positions for the Al and P atoms in the framework were immediately apparent from the different bond distances, ca 1.78 and 1.55Å respectively. The cobalt content for each structure was refined and the final values came to 15.12% and 21% for the 15 and 20% cobalt substitution respectively (substitution figures at synthesis stage). The final R-factors for both refinements were acceptable for a framework material with template molecules occluded in the pores, which have a relatively high level of thermal motion. Crystallographic details for each refinement are given in Table 14.

The space group was forced down from $R\bar{3}$ to R3 to remove the inversion centre. A previous study of the structurally similar CoAPSO-44 material had found the symmetry of the as-prepared material to be $P\bar{1}$ with a lowering of symmetry seen in the double six-rings. Attempts were made to refine this structure in this space group and resolve fully the template and cobalt ordering within the system; however, no satisfactory results were obtained. It is noted that, in the CoAPSO-44 structure solution, K^+ ions were included in the synthesis, and these were found to reside between the template molecule and adjacent double six-rings. This difference can be attributed to the slight distortion of the framework caused by the increased strain imparted on the framework by the K^+ ions.

3.5.1. Single-crystal study of 15% cobalt in CoAlPO-34

The reduction in symmetry has clearly shown that the second template suggested in the initial analysis is no longer present and it was just the symmetry equivalent with the triethylamine disordered over the two sites within the cage, instead the template occupies one site exclusively and not two simultaneously. The structural model for the 15% CoAlPO-34 is shown in Fig.18 with the

Table 11. Final agreement factors for the 25% CoAlPO-34 composition

R Factor	Value
Profile, (R_p)	0.248
Profile, Weighted, (wR_p)	0.145
Profile, Statistically Expected, (R_e)	0.115

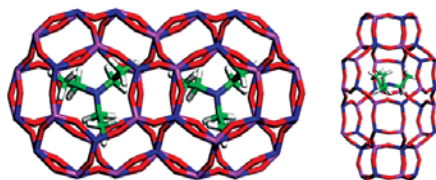

Fig.15. View of the 25% CoAlPO-34 structure showing the position of the single triethylamine template molecule.
The Al/Co sites are shown in blue

Table 12. Atom x, y, z coordinates and isotropic displacement parameters for the as prepared 25% cobalt inclusion. The cobalt occupancy here refines to 22.3%

Atom	x	y	z	Occupancy	U _{iso}
P1	0.44519	0.34279	0.22306	1.00000	0.87196
Al1	0.67061	0.56453	0.23484	0.77637	1.32738
Co1	0.67061	0.56453	0.23484	0.22313	1.32738
O1	0.54072	0.45600	0.19719	1.00000	1.98367
O2	0.35017	0.31757	0.16043	1.00000	1.98367
O3	0.47553	0.25181	0.21206	1.00000	1.98367
O4	0.40997	0.33967	0.31989	1.00000	1.98367
N1	0.66670	0.33330	0.64072	0.33333	3.79955
C1	0.67604	0.23430	0.67234	1.00000	3.79955
C2	0.74936	0.26420	0.75869	1.00000	3.79955

Table 13. Selected bond lengths and angles for the as-synthesised 25% CoAlPO-34 framework

Atom Pair	Bond Length (Å)	Bond Angle	Degrees
P1 - O1	1.51	O1 - P1 - O2	106.8
P1 - O2	1.50	O1 - P1 - O3	111.7
P1 - O3	1.51	O1 - P1 - O4	112.1
P1 - O4	1.51	O2 - P1 - O3	108.2
		O2 - P1 - O4	110.7
		O3 - P1 - O4	107.1
Al1 - O1	1.75	O1 - Al1 - O2*A	106.6
Al1 - O2*A	1.74	O1 - Al1 - O3*A	108.0
Al1 - O3*A	1.83	O1 - Al1 - O4*A	114.2
		O2*A - Al1 - O3*A	110.2
		O2*A - Al1 - O4*A	107.6
		O3*A - Al1 - O4*A	110.0
		P1 - O1 - Al1	142.3
		P1 - O2 - Al1*A	153.1
		P1 - O3 - Al1*B	146.1
		P1 - O4 - Al1*C	147.7
N1 - C1	1.51	C1 - N1 - C1*A	110.4
C1 - C2	1.55	N1 - C1 - C2	110.4

20% data shown in Fig.19. The final atomic coordinates are given in Tables 15 and 16 for the 15% and 20% CoAlPO-34 structures respectively.

Hydrogen atoms located on the organic template molecule were given idealised positions using the HFIX/AFIX commands within SHELX. All the other atoms, as is the case for both refinements, were refined with anisotropic displacement parameters with no constraints. Fractional co-ordinates and U_{iso} for the 15% cobalt structure are given in Table 15.

3.5.2. Single-crystal study of 20% cobalt in CoAlPO-34

Further to resolving the number and location of the template molecules within the structure, distinct cobalt ordering was also found. The cobalt in these systems substitutes on the aluminium T sites located on the bottom of the double six-rings, shown in Fig.20.

3.6. High-resolution powder diffraction data

The structure was again refined as described above using XRS-82, but this time from a starting model in the space group R3. This reduction doubles the T atom site refinement and also shows some cobalt ordering within the system. The final refined unit cell parameters were $a = 13.832$ and $c = 14.933$. The final model was refined to convergence, producing final agreement factors given in Table 18. The observed, calculated and difference profiles are shown in Fig.21.

With the lower symmetry the difference electron density map was generated as before in order to locate the template molecule. The map clearly showed the presence of only a single template molecule in the framework. This was added to the model and the refinement taken to completion. A second map was generated to check for any residual electron density unaccounted for. This final map confirmed only one organic molecule in the structure, as no large electron density peaks were discovered. The final structural model is presented in Fig.22. The final agreement R-factors are given in Table 17. Again we see similar cobalt ordering from the HRPD data to that found in the single

Table 14. Crystallographic details for CoAlPO-34

Cobalt Concentration	15%	20%
Chemical formula	$C_{0.86}Al_{0.73}Co_{0.13}N_{0.14}O_{3.43}P_{0.86}$	$C_{0.86}Al_{0.70}Co_{0.16}N_{0.14}O_{3.43}P_{0.86}$
Formula weight	121.02	121.69
Temperature	150(2)K	150(2)K
Wavelength	0.6872Å	0.6872Å
Crystal system, space group	Trigonal, R3	Trigonal, R3
Unit cell parameters	$a = 13.837(2) \text{ Å}$ $\alpha = 90^\circ$ $b = 13.837(2) \text{ Å}$ $\beta = 90^\circ$ $c = 14.765(3) \text{ Å}$ $\gamma = 120^\circ$	$a = 13.808(2) \text{ Å}$ $\alpha = 90^\circ$ $b = 13.808(2) \text{ Å}$ $\beta = 90^\circ$ $c = 14.881(3) \text{ Å}$ $\gamma = 120^\circ$
Cell volume	$2448.2(7) \text{ Å}^3$	$2457.2(8) \text{ Å}^3$
Z	21	21
Calculated density	1.724 g/cm^3	1.727 g/cm^3
q range for data collection	$2.1^\circ - 29.3^\circ$	$2.2 - 30.5^\circ$
Completeness to $q = 29.3^\circ$	93.3%	94.8%
Reflections collected	5693	5926
Independent reflections	2552 ($R_{\text{int}} = 0.1339$)	3014 ($R_{\text{int}} = 0.1409$)
Reflections with $F^2 > 2\sigma$	2,168	2,138
Structure solution	direct methods	direct methods
Final R indices [$F^2 > 2\sigma$]	$R1 = 0.0706$, $wR2 = 0.1954$	$R1 = 0.0754$, $wR2 = 0.2007$
R indices (all data)	$R1 = 0.0772$, $wR2 = 0.2042$	$R1 = 0.0985$, $wR2 = 0.2192$
Goodness-of-fit on F^2	1.034	1.033
Largest and mean shift/su	0.000 and 0.000	0.029 and 0.025
Largest diff. peak and hole	1.26 and -0.79 e	0.76 and -0.82 e Å^{-3}

Refinement method Full-matrix least-squares on F^2

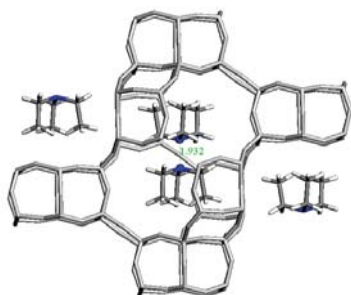


Fig. 16. The N... N separation distance for the crystallographically equivalent template molecule located either side of the centre of inversion. This distance is measured at 1.932Å for the 10% cobalt material

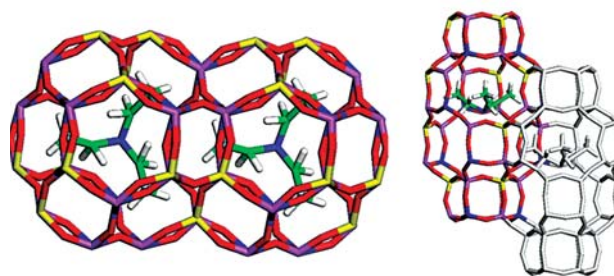


Fig. 18. View of the 15% CoAlPO-34 structure refined in R3. 2 views of 2 cage units are shown for clarity, and to show clearly the template location and orientation. There is only one template molecule per cage

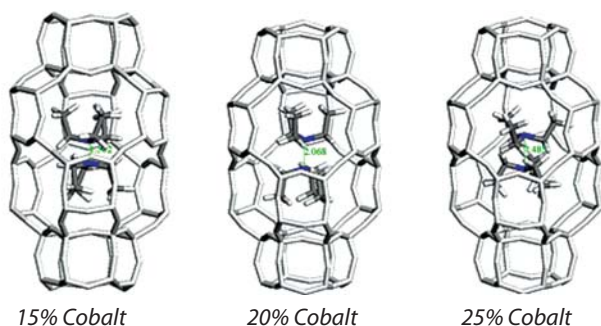


Fig. 17. N... N separation distances of 1.502Å, 2.068Å and 2.485Å for 15%, 20% and 25% substituted CoAlPO-34 respectively

-crystal analysis, with the cobalt selectively substituting for aluminium on only the bottom of the double six-rings (Fig.23). The atomic coordinates, occupancies and displacement parameters are shown in Table 18.

3.7. Effect of cobalt concentration on cell parameters

As the incorporation of cobalt into the aluminophosphate framework in place of aluminium increases, as well as putting a strain in the structure, we would also expect the inclusion of a greater amount of the template acting as a charge balance. The framework strain is due to the differing bond lengths between aluminium and cobalt. For each substituted cobalt, four Al-O bonds (1.73Å) are replaced by four much longer (1.94Å) Co-O bonds. This cobalt inclusion into the aluminophosphate framework has been shown to have adverse effects, and can lead to the collapse of the structure upon calcinations once the template is removed [15].

Table 15. Fractional x, y, z coordinates, U_{iso} and occupancy for as-prepared 15% CoAlPO-34 material.
Note the Cobalt substitution refined to 15.7%

Atom	x	y	z	U_{iso}	Occupancy
P1	1.22875(14)	0.22330(13)	1.02728(9)	0.0236(4)	1
P2	1.55892(13)	0.66163(13)	0.91215(10)	0.0236(5)	1
Al1	1.00445(13)	0.22897(13)	1.03231(9)	0.0222(7)	0.686
Co1	1.00445(13)	0.22897(13)	1.03231(9)	0.0222(7)	0.314
Al2	1.32917(12)	0.43799(12)	0.90759(10)	0.0242(6)	1
O1	1.1100(5)	0.1953(5)	1.0132(4)	0.0444(15)	1
O2	1.3096(4)	0.3222(4)	0.9725(4)	0.0429(13)	1
O3	1.4574(4)	0.5529(4)	0.9407(4)	0.0408(13)	1
O4	1.2227(5)	0.4699(5)	0.9334(4)	0.0404(13)	1
O5	1.5850(5)	0.6585(5)	0.8140(4)	0.0475(16)	1
O6	1.6547(4)	0.6787(5)	0.9733(4)	0.0489(15)	1
O7	1.2619(6)	0.2584(6)	1.1259(4)	0.0475(16)	1
O8	1.2459(5)	0.1258(5)	1.0042(4)	0.0484(16)	1
N1	1.0000	0.0000	0.671(7)	0.44(7)	0.333
C1	1.121(3)	0.082(3)	0.719(3)	0.34(3)	1
C2	1.234(5)	0.116(4)	0.7775(19)	0.43(4)	1

Table 16. Fractional x, y, z coordinates U_{iso} and occupancy for as-prepared 20% CoAlPO-34 material.
Note the cobalt concentration refined to 17.4%

Atom	x	y	z	U_{iso}	Occupancy
P1	0.89214(9)	0.32821(8)	1.23175(7)	0.0251(3)	1
P2	1.32743(8)	0.43581(8)	1.34911(6)	0.0240(3)	1
Al1	0.89633(7)	0.55975(8)	1.22765(6)	0.0261(3)	0.652
Co1	0.89633(7)	0.55975(8)	1.22765(6)	0.0261(3)	0.348
Al2	1.10314(8)	0.44224(8)	1.35520(6)	0.0207(3)	1
O1	0.7811(2)	0.5717(3)	1.2627(2)	0.0406(9)	1
O2	1.0068(2)	0.6553(3)	1.2939(2)	0.0410(9)	1
O3	0.8624(2)	0.4176(3)	1.2494(2)	0.0398(9)	1
O4	0.9819(3)	0.3462(3)	1.2946(3)	0.0510(12)	1
O5	1.2127(3)	0.4207(3)	1.3304(3)	0.0513(12)	1
O6	1.4210(3)	0.5559(3)	1.3339(3)	0.0545(13)	1
O7	1.3321(3)	0.4045(4)	1.4458(2)	0.0458(11)	1
O8	0.9212(4)	0.3235(3)	1.1343(2)	0.0492(12)	1
N1	1.0000	0.0000	1.239(3)	0.40(3)	0.333
C1	1.079(2)	0.1390(10)	1.2399(17)	1.00(3)	1
C2	1.1172(12)	0.2213(17)	1.1490(8)	0.301(12)	1

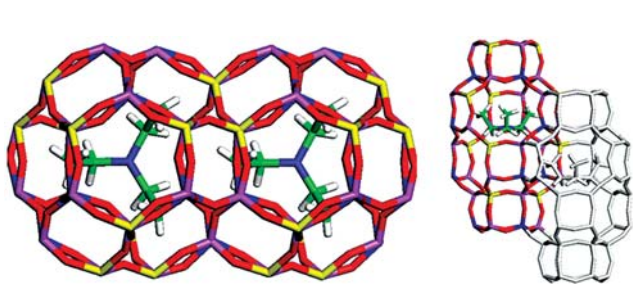


Fig.19. Views of the 20% CoAlPO-34 structure refined in R3. 2 views of 2 cage units are shown for clarity, and to show clearly the template location and orientation. Again only one template molecule per cage is found, as seen with the 15% cobalt sample

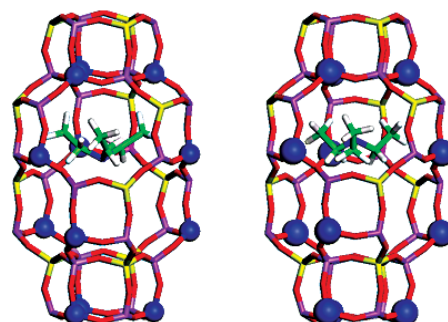
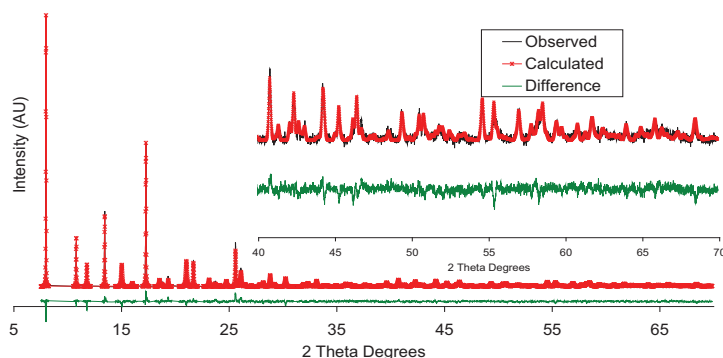
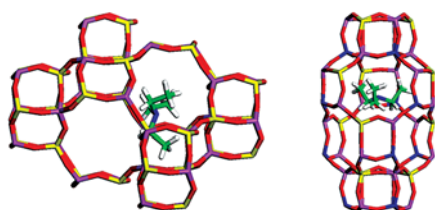


Fig.20. Distinct cobalt ordering can be seen in both the 15 (left) and 20% (right) cobalt samples, where the cobalt substitutes for aluminium in only one of the double six-rings

Table 17. Final agreement factors for the 20% CoAlPO-34 material, in the lower symmetry space group R3

R Factor	Value
Profile, (R_p)	0.269
Profile, Weighted, (wR_p)	0.163
Profile, Statistically Expected, (R_e)	0.156

**Fig.21.** HRPD data for the 20% CoAlPO-34 material refined in the lower space group R3. Showing the best fit between calculated and observed XRD patterns employing XRS-82. Collected at station 2.3, SRS, Daresbury Laboratory using a wavelength of 1.300291Å**Fig.22.** Views of 20% CoAlPO-34 structure refined in R3. The template location is shown clearly, confirming only one template molecule per cage**Table 18.** Atom x, y, z coordinates and isotropic displacement parameters for the as-prepared 20% CoAlPO-34 material. The cobalt occupancy here refines to 20%, i.e a Co:Al site ratio of 1:5

Atom	X	Y	Z	Occupancy	U _{iso}
P1	0.44312	0.34092	0.22437	1.000	0.13048
P11	0.66598	0.55806	0.44402	1.000	0.13048
Al1	0.66816	0.56288	0.23265	1.000	0.87540
Al11	0.44436	0.34122	0.43552	0.666	0.87540
Co11	0.44436	0.34122	0.43552	0.333	0.87540
O1	0.54532	0.44984	0.18927	1.000	0.24889
O11	0.78312	0.57832	0.45904	1.000	0.24889
O2	0.34454	0.31510	0.16780	1.000	0.24889
O21	0.64840	0.63339	0.50696	1.000	0.24889
O3	0.46439	0.24220	0.21888	1.000	0.24889
O31	0.58359	0.43860	0.46695	1.000	0.24889
O4	0.41930	0.35605	0.32117	1.000	0.24889
O41	0.65088	0.58198	0.34616	1.000	0.24889
N1	0.66670	0.33330	0.72844	0.333	3.79955
C1	0.74622	0.29823	0.75922	1.000	3.79955
C2	0.79239	0.26784	0.67595	1.000	3.79955

In this work, however, we are comparing the level of template inclusion within the structure against the substituted cobalt concentration; instability upon calcination is therefore of little concern. Four different cobalt concentrations have been presented, and all studies have shown the inclusion of only one template within the chabazitic cage at all these varying concentrations. The cell parameters and the volumes obtained are shown in Table 19.

Although the cell dimensions change, particularly the c axis, there is an insignificant change in the cell volume. We would expect to see some increase in cell volume if two template molecules were to be included at higher Cobalt concentrations. The cell volume here remains almost constant, suggesting only minor changes to accommodate the larger cobalt loading on the framework and not the gradual introduction of a second template molecule to the chabazitic cage.

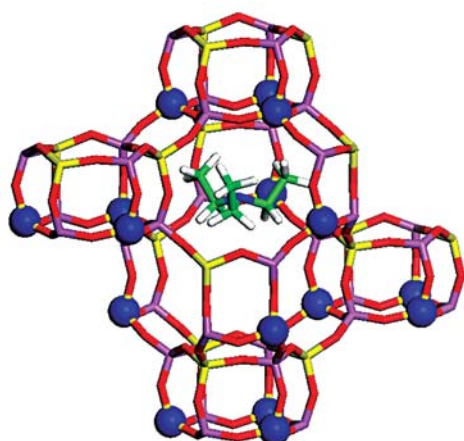
4. Conclusions

From the range of samples produced we were able to collect high quality data both from HRPD and a limited concentration range with microcrystal diffraction. From this we found evidence both in the original $R\bar{3}$ space group and the subsequent reduction to R3 that only a single triethylamine template molecule was occluded within the cages.

The template molecule was quite easily found in the density map as it was not badly disordered, unusual for these systems as the template normally has a high thermal motion. However, it is clear that the template does partially occupy two sites within the chabazitic cage, but not at the same time due to the separation distance between the two nitrogen atoms. Lowering the symmetry confirms this. In the work by Lewis et al [16] it was stated that, with the triethylamine template, the Chabazite phase is only likely to form when the Co:T site ratio reaches 1:6, this in turn gives 2 templates. However the ratio in this work is around 1:12 Co:T sites and we find only one template molecule in the as-prepared phase pure Chabazite. Some cobalt ordering was discovered in the double

Table 19. Cell parameters and volumes for CoAlPO-34 structures with differing substituted cobalt concentrations

Co concentration (%) At synthesis	Co concentration % Refined	a/Å	c/Å	Volume/Å ³
10	8.9	13.858	14.872	2473.4
15	16.6	13.832	14.921	2472.3
20	19.62	13.831	14.933	2473.9
25	22.31	13.832	14.932	2474.1


Fig.23. View of the structure refined in R3. The cobalt ordering is highlighted as blue spheres

six-rings, and was highlighted once the symmetry had been lowered to the space group R3. We see the cobalt substituting for aluminium only on the lower of the double six-rings. Efforts to resolve this further in P1 produced no satisfactory results. To conclude, this systematic study over a range of triethylamine templated CoAlPO-34 materials does provide more evidence for the inclusion of only 1 triethylamine molecule per cage. We found only a single template molecule within the cage and no significant change in cell dimensions or volume, which could indicate changes like the inclusion of a second molecule.

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SYNTHESIS OF CRUDE OIL POUR POINT DEPRESSANTS VIA POLYCONDENSATION OF CASHEW NUT SHELL LIQUIDS

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Summary

The polycondensation of cashew nut shell liquid (CNSL) with formaldehyde was carried out in order to synthesise a pour point depressant (PPD) for paraffinic crude oils. Experimental results showed that the obtained CNSL-formaldehyde novolac resin gave good performance, decreasing the pour point of crude oil by as much as 15°C. In addition, it was also showed that there is an optimum molecular weight value of the synthesised polymer, with which the ability for depression of pour point of crude oil is expected as maximum. Thus, it is believed that with proper molecular weight control, CNSL could be polymerised into a good PPD for local crude oil.

Key words: Pour point depressant, paraffinic crude oil, cashew nut shell liquid, polycondensation, novolac resin.

1. Introduction

With a high content of paraffin, c.a. 17 - 30wt%, of which 50% or more are high (solid) paraffin, Vietnamese crude oil is classified as paraffinic crude oil and has a high pour point, typically in the range of 27 - 38°C. This high pour point may cause some serious problems in production, transportation, and storage; and pose the need for use of an effective pour point depressant (PPD) additive. In general, a PPD is a high molecular weight substance that may effectively disperse and hinder the growth of oil's paraffin crystals when adsorbing on them. Ideally, the structure of PPD consists of (i) a paraffin-like part, which can co-crystallise with paraffin components of crude oil; and (ii) a polar part, which limits the level of co-crystallisation [1, 2]. Copolymers of alkyl acrylates and maleic anhydride are common PPDs used in practice [3 - 5].

Cashew nut shell liquid (CNSL) is a cheap, renewable and abundantly available raw material in Vietnam as it is a by-product of the cashew industry. The chemical composition analysis of typical CNSL [6] (Table 1) shows that it contains a major part of anacardic acid and cardol, which can act as reagents for a variety of reactions for the manufacture of a large number of

products, including inhibitors, detergents, dispersants, and EP additives [7].

It is widely accepted that anacardic acid with proper thermal treatment yields four types of cardanols, which almost have the ready-made chemical structure of an additive. The chemical structures of cardanols found in CNSL are shown in Fig.1 [8]. It is observed that the C15 linear side chains of cardanols offer excellent solubility in

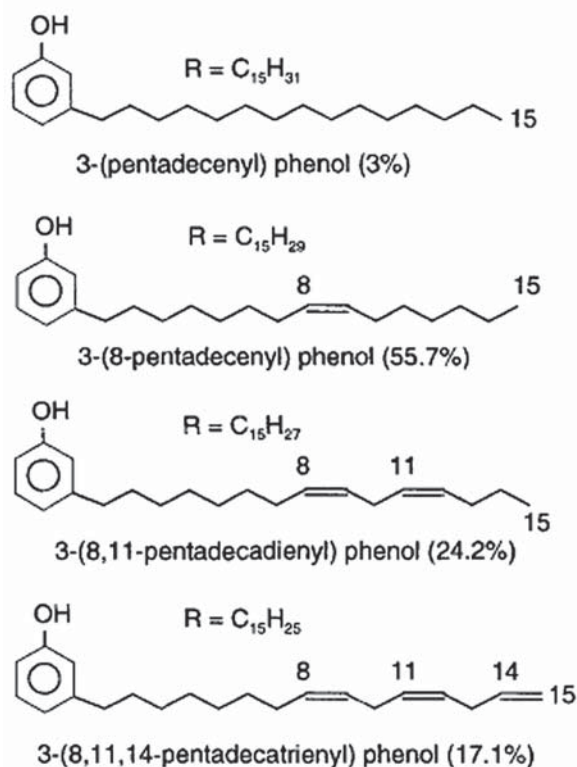


Fig.1. Cardanols obtained from distillation of anacardic acids in CNSL

Table 1. Typical chemical composition of CNSL

Component	Content in CNSL (%)
Cardanol (%)	1.20
Cardol (%)	11.32
2-methyl cardol (%)	2.04
Polymer (%)	20.30
Anacardic acid	64.93

diesel oils and light lubricating oils, and the strongly polar phenol group will induce anti-oxidant characteristics.

The cardanols in CNSL can react with formaldehyde, in the presence of an acidic catalyst, to form a novolac type resin, which has the typical chemical structure as described in Fig.2. Having an ability to disperse paraffin molecules [7], these resins could be good PPDs for paraffinic crude oil. The synthesis of novolac type resin from cardanol and formaldehyde is well documented in relevant literatures [9, 10]. Starting from CNSL, after thermal treatment to convert anacardic acids to cardanols, ideally, a vacuum distillation step is carried out to produce pure cardanol for use in polycondensation reactions. However, this makes the whole process more complex and costly in terms of technology and energy demand. Therefore, in our study, novolac type resins are prepared directly from thermally treated CNSL. This paper presents the preliminary results of our research on polycondensation reactions, and the performances of the obtained products on the depressions of Vietnamese (paraffinic) crude oil's pour point.

2. Experiment

2.1. Synthesis of CNSL- formaldehyde novolac resin

CNSL was first decarboxylated by heating in order to convert most of its anacardic acid component to cardanol. The decarboxylated CNSL (*deca-CNSL*) was then directly used as starting material in the synthesis of novolac type resin described below. The results of acidic value analysis show that the content of cardanol in the obtained deca-CNSL is 79.3 - 80.2wt%.

Novolac resins were prepared from deca-CNSL and formaldehyde with oxalic acid as catalyst, with the cardanol to formaldehyde molar ratio varying from 1:0.4 to 1:0.95. The amount of oxalic acid catalyst used was 0.25mol% based on the amount of cardanol. Polycondensation was carried out in dimethylformamide (DMF) solvent. Typically, 63g deca-CNSL, a pre-calculated amount of paraformaldehyde, 0.05g of methyl hydroquinone (MEHQ) and 0.5g oxalic

acid were fed into a 500ml four-necked flask fitted with contact thermometer, stirrer, dropping funnel and water separator. With stirring and nitrogen blanketing, the reaction mixture was heated to 120°C. Samples were taken after 90 min. of reaction time for viscosity measurement in order to evaluate the progress of polymerisation.

2.2. Analysis of products

Ubbelohde capillary viscometer (SYD-265B Petroleum Products Kinematic Viscosity Tester) was used for viscosity measurement at 40°C.

CNSL-based polymers were analysed by GPC (Agilent 1100 GPC) to determine the average molecular weights of starting materials and the polymer products obtained. Mic A separation column with capillary size of $5 \times 10^2 - 10^5 \text{ \AA}$ was used for measurement at 30°C.

FTIR (Bruker-Equinox55) measurement was carried out for polymer products to confirm the structure of novolac resin. Samples were applied as thin layers on KBr pellets, and scans were performed in the wavenumber range of 4,000 - 400 cm^{-1} .

2.3. Determination of pour point of FO and FO/PPD mixtures

The *deca-CNSLs* and polymers were used for decreasing pour point of Su Tu Den crude oil, which contains 23.6% n-paraffin of $C_{10} - C_{40}$ [11], and has a measured pour point of 27°C. Each PPD product was mixed with various solvents to form 50wt% PPD solutions. The PPD solution was then mixed with crude oil to reach the final content of PPD in the mixture of 0.5wt%. After that, pour points of the mixtures were determined in accordance with ASTM D97. "Blank PPD solution" containing only solvent was also prepared and tested in order to exclude the pour point decreasing effect of pure solvent.

3. Results and discussion

3.1. Decarboxylation of CNSL

Basically, the decarboxylation process leads to a decrease in acidic value of CNSL. Two parameters affecting this process are temperatures and treating times. Fig.3 presents changes of acidic value of CNSL at different temperatures and treating times. It is clear to see that 160°C and 60 mins are the most appropriate temperature and treating time, respectively. Another important point is that the treating time should not exceed 60 mins, since the prolonged thermal treatment will induce polymerisation

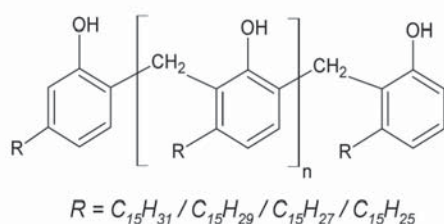


Fig.2. Typical chemical structure of CNSL-formaldehyde novolac resin

of CNSL. Fig.4 shows the variation of viscosity of CNSL with temperatures at different durations of treatment. As the decarboxylation proceeds, the viscosity of CNSL gradually declines due to lower viscosity of cardanol compared to that of anarcadic acid [12]. However, after about 60 mins, a slight increase of viscosities could be observed at all temperatures.

3.2. Synthesis of CNSL-formaldehyde novolac resin

As for the polycondensation of deca-CNSL to form novolac type resin, it was observed during the experiment that the reaction was exothermic, with relatively fast increase in viscosity of the product. Even though methyl hydroquinone was used to prevent self-polymerisation of unsaturated alkyl side chains of CNSL, the viscosity of the reaction mixture was found to hugely increase after 2 hours of reaction time, which was calculated after the addition of the final drop of formaldehyde. This seems to suggest that the polymerisation of CNSL side chains is inevitable as the polycondensation is prolonged at high temperature. Since it was aimed to determine the effect of the polycondensation product in decreasing the pour point of crude oil, only the sample products obtained before 2 hours of reaction were further used for pour point measurements.

FTIR spectrums of deca-CNSL and the product obtained by polycondensation are shown in Fig.5. It can be observed from Fig.5 that new characteristic peaks appear at wavenumbers $1,640\text{cm}^{-1}$ and $1,614\text{cm}^{-1}$; and the shift and deformation of peak at $1,076\text{cm}^{-1}$ (for deca-CNSL) to $1,094\text{cm}^{-1}$ (for the product) which are due to the $\text{C}=\text{O}$ stretching from methylol groups. At the same time, the peaks at $3,010\text{cm}^{-1}$, $1,590\text{cm}^{-1}$ and 778cm^{-1} all remain unaffected. All these facts are identical with those given in previous studies [13] and indicate that the polymerisation has occurred via substitution of methylol groups rather than through the double bonds of the side chains.

During the polycondensation, with increasing content of paraformaldehyde, the viscosity of the reaction mixtures was found to increase (Fig.6), which means the molecular weight of obtained novolac resins increases. GPC measurement results reveal that molecular weights increase from 350g/mol to $9,000\text{g/mol}$ and $25,000\text{g/mol}$, for the reaction mixtures with the CNSL/paraformaldehyde ratio of 1:0.4 and 1:0.9, respectively. The significance of these results is that the molecular weight of the novolac resin product could be effectively controllable with varying ratios of the reactants.

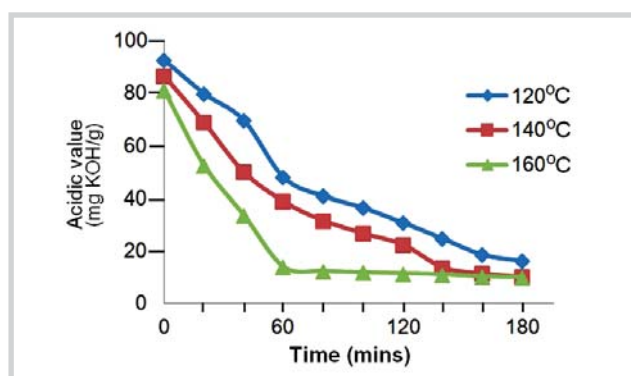


Fig.3. Variation of acidic value of CNSL with temperatures and time of decarboxylation process

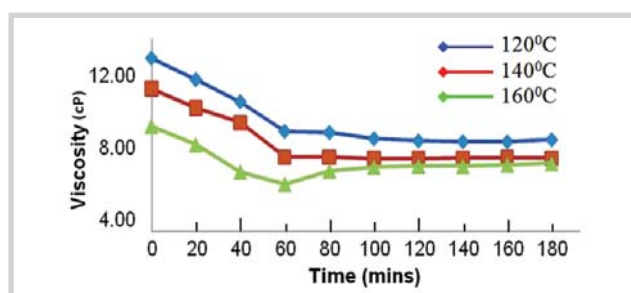


Fig.4. Variation of viscosity of CNSL with temperatures and time of decarboxylation process

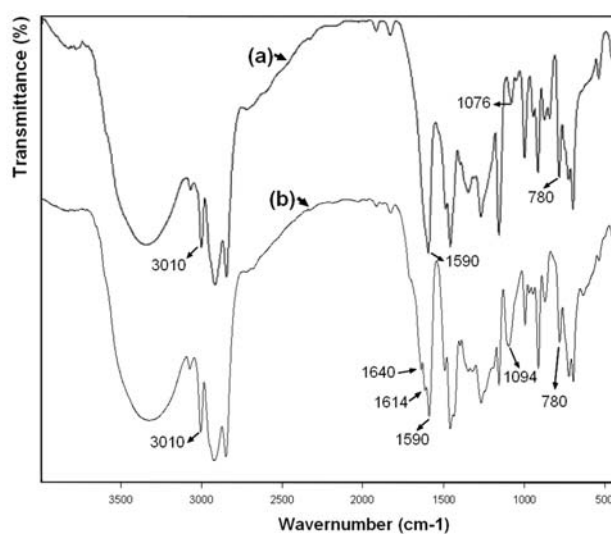


Fig.5. FTIR spectrums of (a) deca-CNSL and (b) novolac resin product

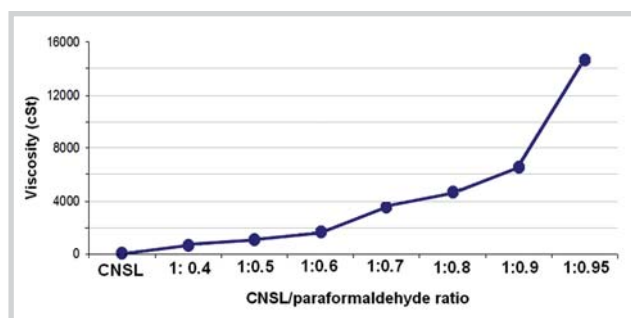


Fig.6. Viscosity of reaction mixture at different CNSL/paraformaldehyde ratios

3.3. Pour point depressing ability of CNSL - formaldehyde novolac resins

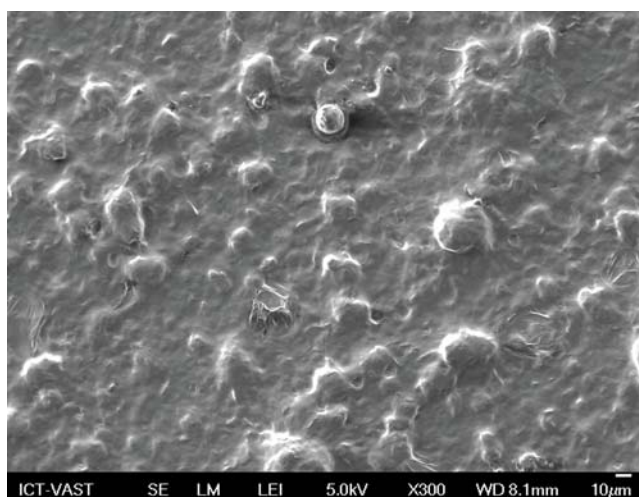
As the direct dissolution of the resin into crude oils is proved to be a difficult process due to poor solubility and high viscosity of the crude oil, CNSL-formaldehyde novolac resins were first dissolved in a specific solvent prior to mixing with the crude oil. The choice of proper solvent is of great importance. A polar solvent (DMF) and a non-polar solvent (xylene) were tested for the dissolution of novolac resins. Table 2 presents the pour point depression capability of different dissolved resins for Su Tu Den crude oil. It could be seen that DMF dissolved resins show significantly better performance compared to xylene dissolved ones. When 0.5% DMF dissolved resin is added to Su Tu Den crude oil, the pour point could drop by 12 - 15°C, whereas a decrease of only 3 - 6°C in pour point of crude oil was observed for xylene dissolved resins. It is also important to notice that the solvents themselves, despite their low freezing points, do not have any pour point depressing ability, as the blank samples have the same pour points as the crude oil. This could be explained by the fact that solvent molecules, with much more smaller size compared to crude oil molecules, could not

prevent the crystallisation and growth of large crystalline of paraffin molecules of the crude oil. Also, the small size molecules cannot induce any spatial arrangement to separate paraffin crystalline or to prevent the formation of a paraffin crystalline network in crude oil.

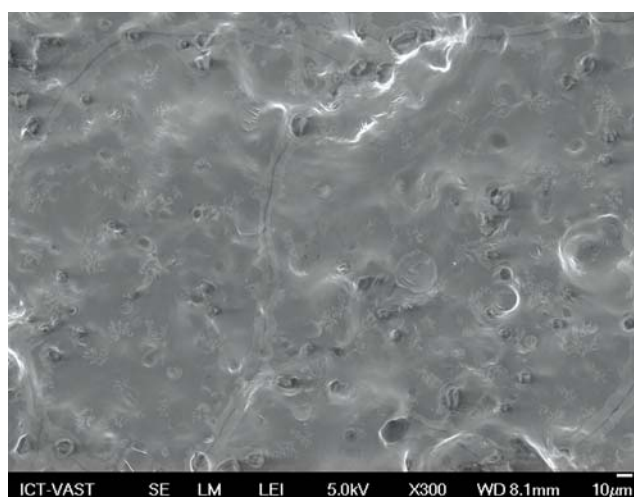
In our previous study, SEM observations of the crystallised surfaces of crude oil/PPD mixtures were carried out and shown in Fig.7 [16]. The surface of crude oil without PPD (Fig.7a) is covered with large paraffin crystals, while in the case of crude oil with PPD (Fig.7b), paraffin molecules seem to be unable to form a network and hardly crystallise, resulting in a smaller size and lower numbers of crystals. This could be attributed to the ability of the PPD novolac resin molecules in adsorbing on and then dispersing the paraffin microcrystallines in the crude oil. Linear alkyl chains of the resins ("R" in Fig. 2) could adsorb on the surface of paraffin microcrystalline, while bulky phenolic groups, connected via methylene bridges, could well separate the microcrystallines apart. As the result, the fluidity of crude oil/PPD mixture is maintained, at much lower temperature, compared to the neat crude oil.

Table 2. Pour point depression ability of different dissolved resins, mixed to Su Tu Den crude oil at 0.5wt%

Solvent	Type of resins	Pour point (°C)	Solvent	Type of resins	Pour point (°C)
DMF	No resin	27	Xylene	No resin	27
	1:0.4 resin	15		1:0.4 resin	24
	1:0.5 resin	15		1:0.5 resin	24
	1:0.6 resin	12		1:0.6 resin	24
	1:0.7 resin	12		1:0.7 resin	24
	1:0.8 resin	12		1:0.8 resin	21
	1:0.9 resin	12		1:0.9 resin	21



(a)



(b)

Fig.7. SEM photographs of surface of (a) freezed neat crude oil and (b) freezed crude oil/CNSL-novolac resin

4. Conclusions

Polycondensation of CNSL with paraformaldehyde, forming novolac resin, seems to be a promising method in production of pour point depressants. CNSL-formaldehyde novolac resins, with a content of 0.5wt%, could reduce the pour point of paraffinic crude oil by 12 - 15°C. It is also worth noticing that the pour point depressing capability of a resin is a function of its molecular weight. This makes the tailoring of resin's molecular weight an effective measure to obtain a PPD of desired ability. Furthermore, the significance of solvent employed to dissolve PPD prior to mixing with crude oil could not be neglected, and further investigations will be carried out to clarify the role of solvent and the mechanism that governs the depression of pour point of the crude oil.

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COMPETITIVE ADSORPTION REMOVAL OF SULPHUR COMPOUNDS IN GASOLINE USING X ZEOLITE

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Summary

The paper presents the results of sulphur removal from gasoline in a ternary system, i.e. benzene, 3-Methylthiophene (3-MT)/Benzothiophene (BT) and isooctane. These results indicate that the presence of aromatic compounds strongly reduces the efficiency of the removal of sulphur in gasoline. Moreover, it is found that the exchanged zeolite exhibits higher activity than the original and the type of sulphur containing compound plays an important role in the adsorption of sulphur in gasoline. A discussion on the obtained results is also presented.

Key words: Adsorption, removal of sulphur, zeolite, gasoline.

1. Introduction

As a positive attempt to cope with the alarming degradation of air quality in today's industrialised world, many environmental regulations have been issued, exerting a great deal of control over the enormous emissions discharged from the relentless operation of billions of transportation means and factories, in which sulphur oxides remain a major concern. Nowadays, most of the sulphur compounds are removed from petroleum-based feedstocks by the hydrodesulphurisation (HDS) process which usually operates at severe conditions, such as elevated temperature (300 - 340°C) and high pressure (20 - 100atm). This process can reduce the sulphur content in gasoline to less than 30ppmw. However, it is difficult to reduce the sulphur content in diesel to less than 15ppmw. In order to enhance the efficiency of the sulphur removal process to meet the required standards, the reactor volume or the catalyst activity must be at least three times larger than those currently used in refineries [1]. Such an increase in the reactor volume will unfavourably affect operating cost and capital. Moreover, another major problem associated with the deep HDS of gasoline is the significant reduction of octane number due to the saturation of aromatics and olefins in naphtha from fluid catalytic cracking, which also means higher hydrogen consumption. Obviously, more effective and affordable methods to produce ultra low levels of sulphur compounds in transportation fuels are needed.

There are several new techniques which have been developed as alternatives to conventional HDS. One of these is the adsorption process, which is considered to be a promising major advanced economical desulphurisation

process due to its ambient operating conditions. However, a great challenge for this approach is to select a suitable sorbent of high selectivity and sulphur capacity. A wide variety of sorbents are commonly used for adsorption purposes such as activated carbon, silica-based sorbents, zeolites, and metal exchanged/impregnated activated carbon/zeolites/mesoporous materials [2 - 5]. Yet the capacity reported was not satisfactorily high. During 2003 and 2004, Hernandez and co-workers [6] found that adsorbents based on Y-Zeolites exchanged with Ni, Cu or Ag cations have good capacity for thiophene adsorption in benzene via strong π -complexation bonding, which is stronger than Van der Waals interaction but can be easily broken by manipulating temperature and pressure.

In our previous study [7], in a binary system, it was found that the concentration of the exchanged metal in the zeolite and the type of sulphur containing compound strongly influenced the removal of sulphur compounds in gasoline. The present study deals with ternary systems of isooctane, benzene, and 3-MT/BT using Ni^{2+} exchanged zeolite as adsorbent.

2. Experimental section

The experimental process was described in detail in [7]. Briefly, batch liquid adsorption experiments were carried out in a 15cm³ vial. The ratio of fuel to adsorbent was fixed at 85 [8] with constant stirring. The equilibrium time was set at 8h [9]. Once the system reached equilibrium, samples were withdrawn by using syringe and then analysed by gas chromatography (HP 5890 Series 2) with FID detector and HP-5 column (30m x 0.32mm x 0.25mm film thickness).

3. Results and discussion

3.1. Effect of aromatic content on sulphur compounds adsorption

As discussed above, in view of large aromatic content (benzene used as the model aromatic compound), we believed that there was a competition between aromatic (benzene) and sulphur (3-MT or BT) compounds getting adsorbed on zeolites. In order to obtain a clearer picture on the effect of aromatics in the desulphurisation of transportation fuels, experiments using a small range of benzene concentration (0 - 15% by weight) in a solution of isooctane and 2,000ppmw (0.2% by weight) sulphur containing compound (3-MT and BT) content were conducted. NiX zeolite with the highest metal loading (7.48%wt Ni) and the original NaX zeolite were chosen for testing. The results are shown in Figs.1 and 2.

Results in Figs.1 and 2 illustrated a dramatic reduction in the sulphur uptake with increasing aromatics

concentration. The drastic drop on adsorption capacity was found to be approximately 85% for 3-MT and 80% for BT at benzene concentration of 6%. As benzene concentration increased further, the further reduction in adsorption capacity was not significant. The influence of aromatic content could be explained from the fact that benzene can compete with 3-MT and BT for entering zeolite pores and adsorbing on the active sites of the zeolite. Even with benzene presented as co-adsorbate, the exchanged zeolite still exhibited a higher affinity towards sulphur compounds than the original one. In other words, the interaction between sulphur compounds and the exchanged zeolite seemed to be ruled by π -complexation. Therefore, it could be safely concluded that the π -complexation sorbent is more favourable in desulphurisation application.

3.2. Competitive adsorption between sulphur compounds and benzene on zeolites

Results for sulphur compounds and benzene adsorption on NiX (7.48%wt Ni) and original NaX zeolites from different concentrations of benzene (0 - 15% by weight) in solution of isooctane and 2,000ppmw sulphur containing compound content are presented in Table 1 and 2 giving more insights about the impact of aromatics on the sulphur removal process. In addition, Table 1 and 2 also show selectivity (given in terms of number of moles of sulphur compounds and benzene adsorbed on zeolites) for sulphur compounds and benzene, helping to estimate how sulphur compounds were more favoured over benzene in mixture solution.

As seen from Table 1 and Fig.3, in case of low aromatic content (2%wt), the selectivity of 3-MT and BT over benzene was 1.40 and 1.37, respectively, for π -complexation sorbent (NiX zeolite). Meanwhile, at this benzene concentration, for original zeolite (NaX), the selectivity was 0.42 for 3-MT and 0.90 for BT. This result confirmed the beneficial effect of exchanged zeolite on the adsorption selectivity of sulphur compounds in the presence of

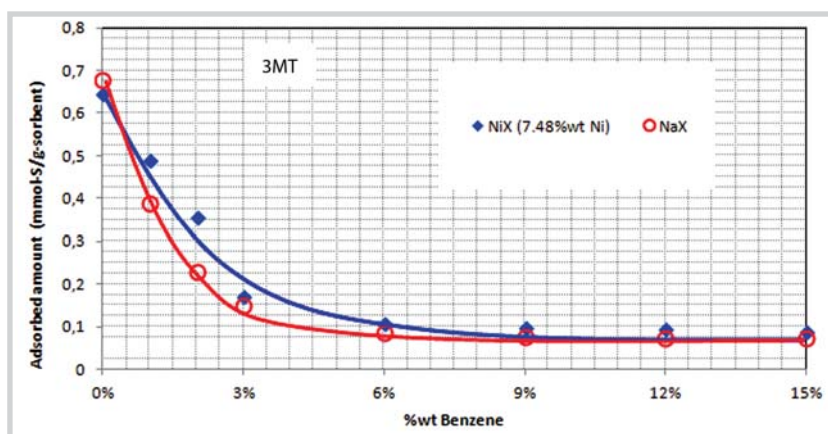


Fig.1. Effect of competitive benzene adsorption on 3-MT adsorption on NiX (7.48%wt Ni) and NaX

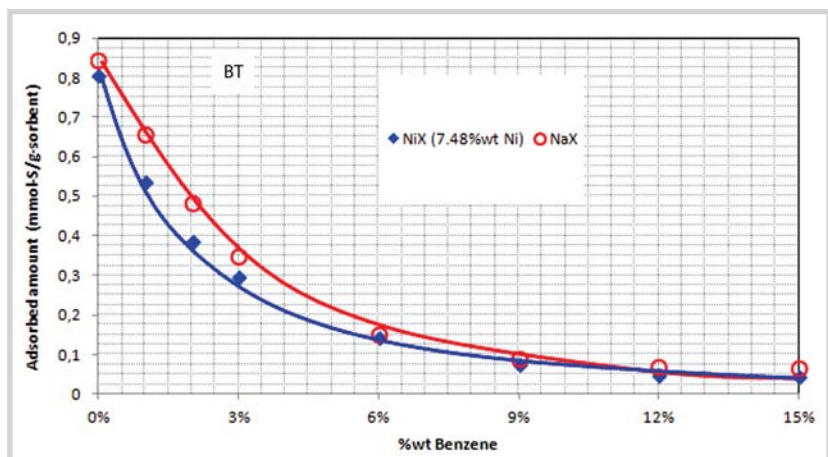


Fig.2. Effect of competitive benzene adsorption on BT adsorption on NiX (7.48%wt Ni) and NaX

Table 1. Selectivity of 3-MT over benzene in ternary system using NiX (7.48%wt Ni) and NaX zeolites

Zeolite	Benzene content (%wt)	Absorbed 3-MT (mmol/g-sorbent)	Adsorbed Benzene (mmol/g-sorbent)	Selectivity ($S_{3MT/Benzene}$)
NiX (7.48%wt Ni)	0%	0.645	-	-
	1%	0.492	0.161	3.06
	2%	0.356	0.254	1.40
	3%	0.173	0.506	0.34
	6%	0.108	0.561	0.19
	9%	0.098	0.549	0.18
	12%	0.095	0.589	0.16
	15%	0.091	0.585	0.16
NaX	0%	0.681	-	-
	1%	0.389	0.298	1.28
	2%	0.230	0.478	0.42
	3%	0.150	0.556	0.27
	6%	0.087	0.594	0.15
	9%	0.078	0.607	0.13
	12%	0.074	0.607	0.12
	15%	0.075	0.635	0.12

Table 2. Selectivity of BT over benzene in ternary system using NiX (7.48%wt Ni) and NaX zeolites

Zeolite	Benzene content (%wt)	Absorbed BT (mmol/g-sorbent)	Adsorbed Benzene (mmol/g-sorbent)	Selectivity ($S_{BT/Benzene}$)
NiX (7.48%wt Ni)	0%	0.842	-	-
	1%	0.657	0.145	4.48
	2%	0.482	0.350	1.37
	3%	0.350	0.475	0.74
	6%	0.150	0.695	0.22
	9%	0.089	0.702	0.13
	12%	0.070	0.768	0.09
	15%	0.065	0.750	0.09
NaX	0%	0.805	-	-
	1%	0.538	0.272	1.95
	2%	0.387	0.422	0.90
	3%	0.298	0.518	0.58
	6%	0.144	0.634	0.23
	9%	0.075	0.718	0.10
	12%	0.048	0.744	0.06
	15%	0.046	0.766	0.06

benzene. The high values of selectivity at low benzene concentration (up to 2%wt) also implied that sulphur compounds have higher strengths of π -complexation bonds than benzene. However, when increasing the aromatic content, experimental data showed a significant decrease of selectivity and an effective shifting of the balance to benzene. These less-than-one values imply that zeolites are more subjective to be occupied by benzene than by sulphur compounds at this high level of benzene concentration. It could be explained that at these concentrations, despite sulphur compound's high strength of π -complexation bonds, the surface of zeolite had been completely saturated by benzene molecules, leaving very few active sites available for sulphur compounds to be bound. However, at any benzene

concentration, the selectivity of sulphur containing compound over benzene of the exchanged sorbent (NiX) is higher than that of the original one (NaX).

Considering the effect of sulphur-containing compound on the removal of sulphur from gasoline (Fig.3, Table 1 and 2), the type of sulphur-containing compounds strongly affected the adsorption capacity of the studied zeolites. As it can be seen, at low concentration of benzene, the adsorbent showed higher selectivity to BT than 3-MT. However, at high concentration of benzene (higher than 6%wt), there was not much difference between the 3-MT selectivity and BT selectivity. This result was in good consistence with our previous results in binary systems where the higher affinity of the aromatic ring played crucial role in the adsorption of S-containing compound.

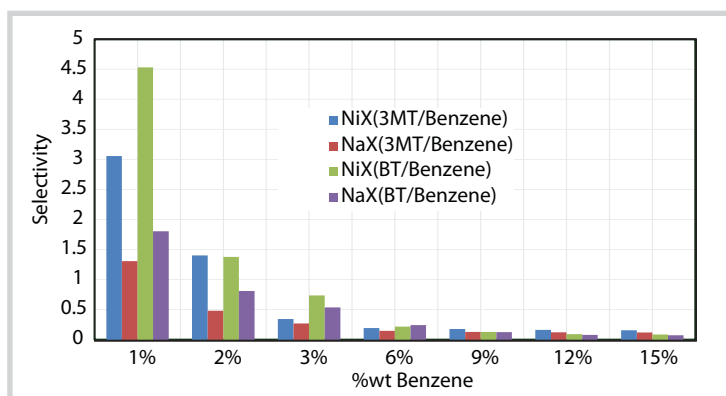


Fig.3. Adsorption selectivity of adsorbents at different benzene concentrations

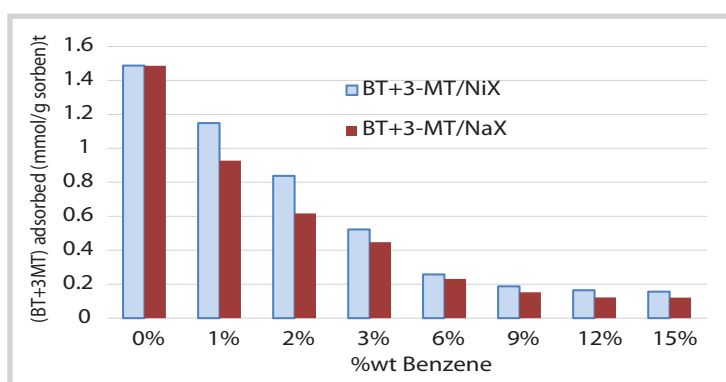


Fig.4. Effect of Benzene adsorption on BT+3MT adsorption on NiX (7.48%wt Ni)

As a first step to illustrate the effect of benzene adsorption on the removal of sulphur-containing compounds in gasoline, the total amount of BT and 3-MT adsorbed on zeolites in the presence of benzene is depicted in Fig.4. It can be seen that, the total amount of BT and 3-MT adsorbed is the same on both zeolites when there is no Benzene in the system. This can be explained by the saturation of adsorbate on the adsorbent because the adsorption time was kept quite long. The benefit of π -complexation in the sorbent (NiX) is observed at any concentration of benzene in the system, especially in the range of 1 to 6 %wt.

4. Conclusions

The presence of aromatic compounds strongly influences the adsorption of sulphur containing compound on NaX and NiX zeolites. The adsorption capacity decreases with increasing benzene concentration. The rate of decrease is especially high at low benzene concentrations (less than 3%). However, when the concentration of benzene reaches a certain level, the rate of sulphur-containing compound adsorption only decreases slightly.

Similar to binary systems, the adsorption of sulphur on the studied zeolites depended on the type of S-containing compounds. The capacity to adsorb BT is higher than 3-MT, which might be the result of higher affinity of the aromatic rings in the BT structure.

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CORPORATE SOCIAL RESPONSIBILITY - COMPARATIVE ANALYSIS FROM PETROVIETNAM AND VINATEX

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Summary

Corporate social responsibility (CSR) is one of the key concepts in the study of mutual relations between business and society. Demand for responsible business behaviour has expanded all over the world in the 21st century. Vietnam as a developing country also has typical motivations and initiatives for CSR. This research aims to explore the CSR perception and practices of Vietnamese companies through the cases of two national groups: the Vietnam National Oil and Gas Group (Petrovietnam) and the Vietnam National Textile and Garment Group (Vinatex), highlighting various concepts and themes such as business ethics, social responsiveness and public policy in order to provide authentic insights into the business philosophy in the country.

Key words: Corporate social responsibility, Petrovietnam, Vinatex, Altruistic CSR, Strategic CSR.

1. Introduction

During the last couple of years, Corporate Social Responsibility (CSR) has become the “new catching phrase” in the business world not only in developed countries but also in developing countries. Its initiatives have been materialised and due to the broad, dialectical concept, there are various definitions of CSR depending on different institutions, organisations and companies but all include numerous of social, environmental and ethical issues:

- “The continuing commitment of business to behave ethically and contribute to economic development while improving the quality of life of the workforce and their families as well as of the local community and society at large” (World Business Council for Sustainable Development).

- “A concept whereby companies integrate social and environmental concerns in their business operations and in their interaction with their stakeholders on a voluntary basis” (The European Commission).

- “Operating a business in a manner that meets or exceeds the ethical, legal, commercial and public expectations that society has of business” (Business for Social Responsibility).

In Vietnam, the government is recently taking up CSR-relevant issues as a public policy area. This research aims to explore how the CSR concept is applied in the

context of Vietnam through the cases of Petrovietnam and Vinatex. Petrovietnam and Vinatex are selected among other national groups because of three criteria: (i) their importance to the national economy; (ii) their utilisation of a wide range of natural resources and social capitals; (iii) scope of activities covering globally (in order to define international impacts on business philosophy related to CSR). The main objectives of the research are to: (i) document their views and perception of CSR; (ii) address the similarities and divergences between CSR principles and approaches; and (iii) examine to what extend social programmes are perceived in the corporate CSR philosophy.

2. Theoretical framework

This section is intended to give concepts and basic assumptions to the important questions as well as suggest the way to make sense of data, and help to connect a single study to the immense base of knowledge [6]. Social contract theory, social justice theory, rights theory, deontological theory and the theory of the triple bottom line are the framework that this research is situated in.

The social contract theory is that a society contains a series of explicit and implicit contracts between individuals, organisations, and institutions. These contracts are evolved so that exchanges could be made between parties in an environment of trust and harmony. According to this, corporations enter into these contracts

with other members of the society, and receive resources, goods, and societal approval to operate in exchange for good behaviour.

The social justice theory focuses on fairness and distributive justice. The theory argues that a fair society is one in which the needs of all its members are considered, not just those with power and wealth. As a result, corporate managers need to consider how these goods can be most appropriately distributed in the society.

The rights theory means that while the shareholders of a corporation have certain property rights, this does not give them a license to override the basic human rights of employees, local community members, and other stakeholders.

The deontological theory deals with the belief that everyone, including corporate managers, has a moral duty to treat everyone else with respect, including considering their needs.

The Theory of the Triple Bottom Line states that it is necessary for a company to take into account not only financial outcomes but also environmental and social performance starting from the base (bottom)

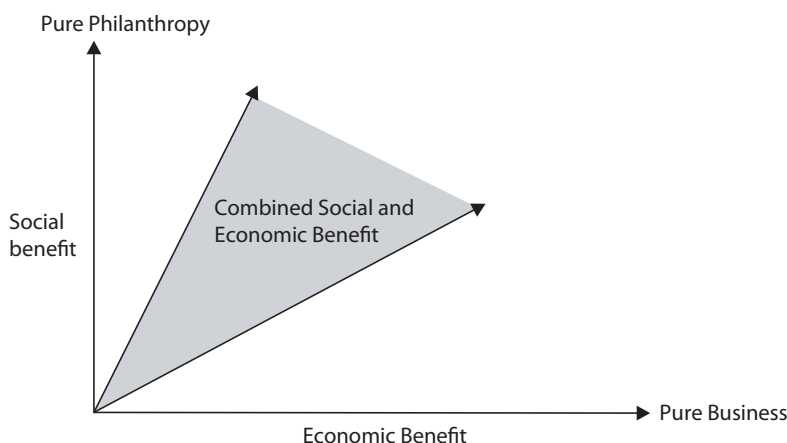


Fig.1. A convergence of interests between business and society [3]

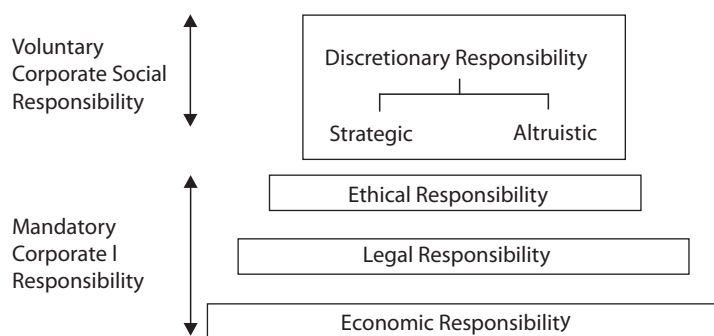


Fig.2. The social responsibilities categories [3]

and three objectives (triple-line) that are social justice, environmental quality and economic prosperity.

The below figure provides a further view on the fact while corporations have always been the “engines” for economic development; they also need to be more proactive in balancing this drive with social benefits.

A multiple corporate social responsibility is conceptualised with a pyramid construct in which the total social responsibilities of business embody the economic, legal, ethical and discretionary categories, with an early emphasis on the economic, legal, ethical aspects as the mandatory responsibilities and later a concern for discretionary factors as in Fig.2 [3].

Economic responsibility entails profitability for shareholders, good jobs for employees and quality products for customers. Legal responsibility refers to compliance with laws and playing by “the rules of the game”. Ethical responsibility involves doing what is right, fair and avoiding harm or mandatory fulfilment of a firm’s economic, legal, and ethical responsibilities. Discretionary responsibility in a voluntary basis consists of (i) Altruistic responsibility-fulfilment of an organisation’s philanthropic responsibilities, irrespective of whether the business will reap financial benefits or not; (ii) Strategic responsibility-fulfilment of philanthropic responsibilities simultaneously benefiting the bottom line.

The above section reviews the CSR initiatives through important theories in order to see the path for the concept to emerge and how it has been reflected in the literature. The latter will discuss the major trends and tries to explore the driving forces beyond CSR practices during the management phase in the two cases.

3. Comparative analysis

Petrovietnam is the leading national group in Vietnam, making an average annual growth of 18 - 20% with a total turnover equal to 20% of the entire country’s GDP and contributing approximately 25 - 30% of the State Budget revenues. Petrovietnam is now focusing on five key areas of operation: oil and gas exploration and production; refinery/petrochemicals; gas industry; power generation and high-quality petroleum

technical services. It is in cooperation with various international petroleum companies in the implementation of 60 petroleum contracts in Vietnam and 17 contracts in 14 countries.

Energy for national development is set as the mission of Petrovietnam and the group identifies its business philosophy respectively to key stakeholders (as in Table 1). This illustrates a crucial point in the company's business due to its strong effects to the decision making process, the management policies taken and the consequential actions undertaken. It also influences the choices of business partners that might work in compliance with Petrovietnam's policy.

Awareness of CSR is being promoted among managers and employees, and underlined to the public as well as the community. Petrovietnam always considers this not only as the political task of the leading national group but also the unique traditional culture of Petrovietnam. A set of policies related to CSR has been systematically established and concretely integrated in the business action plans via (i) co-operation programmes with provinces, cities, ministries and government agencies, (ii) internal legal documents, annual reports, and CSR reports; and (iii) the yearly approved budget (with hundreds of billions VND). Together with effective production and business operations, Petrovietnam has contributed 1752.3 billion VND to the social security programmes in 2011 - 2013 period.

Vinatex was established in 1995 as a complex owned by companies including the Vietnam Textile and Garment Group (the mother company), the centres for research

and training and nearly 120 sub-companies. These sub-companies are joint stock companies doing business in different fields, e.g. producing textile and garments and providing commercial services. They also have their distribution systems including wholesaler and retailers. Vinatex has had a commercial relationship with more than 400 corporations and companies from 65 countries and territorial regions. Its export value has accounted for over 20% of the total export turnover of the Vietnamese textile and garment industry. The average growth rate is 10% per year, its export value is more than one billion USD in 2011 and the income is approximately 1.8 billion USD [15].

In recent years, Vinatex has been seeking for feasible solutions in order to enhance business efficiency. Among these, integrating CSR into its development strategy is considered as the competitive factor to call for overseas importers because this concept is gaining acceptance among trading partners and investors, adhering to international agreements and the global society. It could be a positive business case for companies in developing countries in the global supply chain.

The following table presents a variety of CSR performance indicators and classifies current CSR programmes in the groups.

4. Discussion

The similarity between the CSR practices of Petrovietnam and Vinatex is their major contribution to the society and economic development is widely recognised. Petrovietnam, for instance, has expanded an integrated gas sector with focus given to the development of the national gas industry infrastructure, especially in the North and the Centre of the country. In the case of Vinatex, setting up new spinning, weaving and knitting, fibre and synthetic factories means creating more jobs and promoting regional production, trade and commerce. Over the years in Vietnam there has been a stable trend for the government to provide benefits and well-fare for the people and the community. Getting involved in the social activities might turn companies into political as well as economic agents [4]. In fact, the two groups have fully implemented mandatory CSR (ethical,

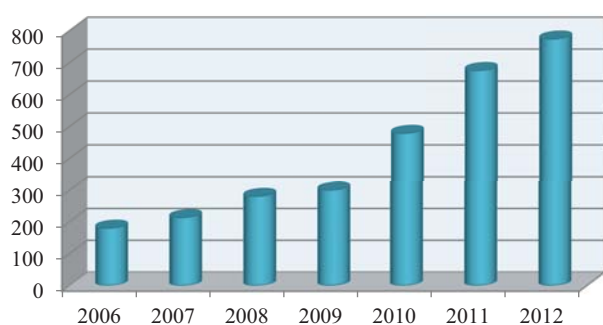


Fig.3. Revenues of Petrovietnam 2006 - 2012 [7]
Unit: thousand billion VND

Table 1. Petrovietnam business philosophy [14]

Society	Take the lead in social welfare and social programmes
Customers and partners	Share profits and responsibilities
Employees	Take care of material and spiritual life of employees
Safety and environment	Safety for the human beings and property, environmental protection and sustainable development

Table 2. CSR programmes and corresponding classification

Company	Example of social programmes	Altruistic vs. Strategic CSR
Petrovietnam	Contribute to government's charitable funds and programmes launched by the Central Committee of Vietnam Fatherland Front, Vietnam Veterans Association, etc.	<i>Altruistic:</i> charitable and in-kind donation themes.
	Partnership to build schools and accommodation for local teachers in the uplands; provide undergraduate/postgraduate scholarships for poor students, excellent students of universities.	<i>Altruistic:</i> educational and learning theme.
	Conduct programmes on clean energy, conversion of salt water into fresh water for island people.	<i>Strategic:</i> Renewable energy/environmental theme.
	Provide financial supports to local communities.	<i>Strategic:</i> Supporting the Anti-Poverty Programmes.
	Build houses of Great Unity, build hospitals, health care centres and medical facilities for local people.	<i>Altruistic:</i> community development theme (Improving access to basic human needs).
	Create jobs for off-springs of former veterans, wounded soldiers, families of national revolutionary martyrs, etc. Establish "Petrovietnam Mutual Assistance Fund" to assist the staff (including retired officers) who face with difficulties, sickness and diseases, etc.	<i>Altruistic:</i> Gratitude theme, corporate culture.
Vinatex	Implement buyer code, international certifications such as SA 8000; ISO 14000, etc.	<i>Strategic:</i> create the trust of customers, partners/competition theme.
	Support the poor in mountainous areas, borders and islands, and disadvantaged families across the country.	<i>Altruistic:</i> charitable and in-kind donation themes.
	Organise family festivals for employees.	<i>Altruistic:</i> corporate culture to create the loyalty/faith of employees.
	Human blood donor, Helmets for kids, etc.	<i>Altruistic:</i> community's health, safety theme.
	Provide Vinatex's products to people in remote/upland areas, launch the "Vietnamese people use Vietnamese goods" campaign.	<i>Strategic:</i> promote potential/target markets, boost domestic consumption.

legal, and economic responsibilities) and voluntary CSR through specific altruistic and strategic themes as their response to a diversity of internal and external pressures from stake holders in the long-term and/or short-term.

On the other hand, different approaches are observed through the spectrum of policies, strategies, missions and core values of these two groups.

The elements of the *Social justice theory* expressing a company's responsibilities to behave ethically on a fairness and distributive basis to protect the environment, improve the quality of life of the employees, the local community and the society are connected with the mission of Petrovietnam. The basics of Petrovietnam's CSR principles are to ensure unity, sharing and mutually assisting community. As a result, it helps to enhance agreements and equality towards a harmonious and civilised society.

Whereas Vinatex has demonstrated susceptibility to market-based CSR pressure that closely links to the *Theory of the Triple Bottom Line*. Joining the global market

does not only bring opportunities (better trade facilities, reduction of tariffs and barriers) but also challenges when international standards are introduced. As a result, companies have to conform to global norms with respect to environment and labour standards. Vinatex with an effort to enhance competitiveness (through CSR programmes) and promote export- oriented business has received orders from top apparel and textile importers (from US, Japan, and EU) and they are estimated to grow approximately 20% year by year. These foreign investors tend to be concerned about the fundamentals (macro-economic performance, governance, and political risks) plus their reputation in markets where high standards are seen as desirable [8]. This is the context in which market driven cycle for CSR is demonstrating how standards can be raised for sound business reasons.

5. Conclusions

In many ways, CSR can be considered as a debate. From the classical economics point of view, the whole economy/society is the place where individuals "freely

pursue their private goals" [1]. The main function of business is to maximise profits and that corporation is not "the right person to solve social problems... such problems should be left to government. Moreover, "violent cities, deteriorating schools, pollution, poverty and other problems are the ingredients of economic stagnation, not corporate welfare" [4]. Another argument is that CSR is "a public relation ploy designed to divert attention away from the destructive social consequences of corporate activities" or it is "driven by certain groups in the West and not the (supposed) intended beneficiaries in the global South" [5] and the conceptualisation might not be relevant to developing countries context.

However, from the liberal perspective, corporations are "social enterprises" to provide goods and services, as well as to secure livelihoods. They are expected to have responsibilities to the society, community development and environmental protection. Besides, corporations are having ever greater impacts on the society as their technological and economic capacities grow. They are not responsible for solving all social problems but for the problems and social issues induced by their activities.

It can be seen in the cases of Petrovietnam and Vinatex that embarking on social responsibility for corporate development strategy implies a new way of doing business to accommodate expectations of the business sector in Vietnam.

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USING NANOCOMPOSITES OF CHITOSAN AND MONTMORILLONITE FOR ADSORPTION OF HEAVY METAL IONS FROM WASTEWATER

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Summary

In this study, chitosan/montmorillonite nanocomposites were synthesised from chitosan and montmorillonite by dispersion of montmorillonite into chitosan solution which was prepared by dissolving the chitosan in an aqueous acetic acid solution. The resulting nanocomposites were characterised by XRD (X-ray diffraction), FTIR (Fourier transform infrared) and SEM (scanning electron microscopy) measurements. Batch equilibrium experiments of Cu (II) (Cu^{2+}) and Cd (II) (Cd^{2+}) ions adsorption were carried out on chitosan/montmorillonite nanocomposites. Models of adsorption isotherms were applied to describe the adsorption isotherms of heavy metal ions by nanocomposite. The relationship between adsorbing capacity (q_e) and equilibrium mass concentration (C_e) is in accordance with the isothermal adsorption equation of Langmuir. Two kinetic models, including pseudo-first-order and pseudo-second-order, were used to analyse the heavy metal ions adsorption process. The pseudo-second-order chemical reaction kinetics provide the best correlation of the experimental data, therefore the adsorption dynamic follows the laws of pseudo-second-order kinetics.

Key words: Chitosan/montmorillonite nanocomposites, copper, cadmium, kinetic, adsorption isotherm.

1. Introduction

Common technologies for heavy metal removal are membrane separation, ion exchange, electro-deposition, and chemical precipitation. These methods prove to be costly and inept, especially in removing trace amounts of heavy metals [2]. Another disadvantage is the production of sludge or mud, which requires proper disposal and confinement [3]. On the other hand, adsorption effectively removes contaminants in wastewater with high solute loadings and even at dilute concentrations ($< 100\text{mg/L}$). Use of natural adsorbents like peat, banana pith, rice hull and chitosan proves to be economical and effective in removing a variety of contaminants [2, 4].

Chitosan contains reactive hydroxyl ($-\text{OH}$) groups and amino ($-\text{NH}_2$) groups that have the potential to bind heavy metals. Pure chitosan tends to agglomerate and form a gel in aqueous media, rendering most of the hydroxyl and amino groups inaccessible for metal binding. Coating chitosan as a thin layer onto an immobilisation support increases the accessibility of its binding sites, and improves the mechanical stability [5, 6]. Montmorillonite has a net negative surface charge and has little or no affinity to anionic, in there, chitosan, a natural biopolymeric cation, is an excellent candidate to modify montmorillonite for the adsorption. Recent research works have shown

that chitosan/montmorillonite composites represent an innovative and promising class of sorbent materials. Gecol et al. investigated the removal of tungsten species from water using chitosan coated montmorillonite biosorbent [7, 8]. Chang and Juang studied the adsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay [9]. However, studies about the removal of heavy metal ions by chitosan/montmorillonite nanocomposites as an adsorbent are very scarce. Therefore, in this study chitosan/montmorillonite (CTS/MMT) nanocomposite was synthesised, characterised, and the adsorption kinetics and isotherms for Cu^{2+} , Cd^{2+} from water solution onto nanocomposite with chitosan and montmorillonite.

2. Materials and method

2.1. Materials

Chitosan of medium molecular weight (average molecular weight $\text{MvZ } 92,700\text{g mol}^{-1}$), used in this work was bought from Aldrich Chemicals. This chitosan was obtained by deacetylation of chitin from crab shells and it had a degree of deacetylation of 80%. Glacial acetic acid (HAC) obtained from Sigma-Aldrich® Co. LLC. was used as the solvent for chitosan. The montmorillonite, with a cationic exchange capacity (CEC) of $92.7\text{mequiv}/100\text{g}$,

was supplied by Sigma-Aldrich®Co. LLC .Analytical grade of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2$ were procured from China.

2.2. Film preparation

Formation of chitosan/montmorillonite nanocomposites: chitosan solution was prepared by dissolving chitosan in a 2% (v/v) aqueous acetic acid solution at a concentration of 2wt% followed by centrifuging to remove the insoluble material. Montmorillonite was first swelled by 50ml distilled water and then added to 50ml chitosan solution with montmorillonite contents of 1 wt% followed by stirring at 60°C for 6 hours. After that, chitosan/montmorillonite solutions were cast on a plastic dish at 60°C for 24 hours. They were termed chitosan/montmorillonite - 1% (1 is concentration of montmorillonite).

2.3. Characterisation of the composite film

IR spectra of the samples were characterised using a FTIR Spectrophotometer (IMPAC-410) in KBr pellets in the range of 4,000 - 400 cm^{-1} . XRD analyses of the powdered samples were performed using an X-ray diffractometer with Cu anode (D8-Advance, Bruker), running at 40kV and 40mA, scanning from 0.5° to 5° at 3°/min. The scanning electron microscope (SEM) were measured using a Hitachi S-4800.

2.4. Adsorption kinetic studies

Single metal solutions of Cu^{2+} , Cd^{2+} were prepared with concentrations of 100mg/L and with pH 5 - 6. The three-necked flask is filled with 0.3g nanocomposite of chitosan/montmorillonite and 30mL of metal solution. The metal solution was agitated using thermostated shaker with a shaking of 200rpm and the pre-determined contact times ranged from 1 min. up to 90 min. The filtrate was analysed using atomic absorption spectroscopy (AAS)

method to determine Cu^{2+} , Cd^{2+} .The adsorption capacity was calculated:

$$q_e = \frac{(C_o - C_e)V}{W}$$

Where:

C_o is the initial metal concentration (mg/L);

C_e is the final or equilibrium concentration (mg/L);

V is the volume of the metal solution (mL);

W is the weight of chitosan/montmorillonite (g).

2.5. Adsorption isotherm studies

Single metal solutions of Cu^{2+} , Cd^{2+} with concentrations of 10 - 120mg/L, were utilised for isotherm studies. The experiments were performed using 0.3g of chitosan/montmorillonite in 30mL of the metal solution in the three-necked flask. Solutions with an initial pH 6 were agitated using a shaking of 200rpm for 90 min. at room temperature.

3. Results and discussion

3.1. IR analysis of nanocomposites

Fig.2 shows the IR spectra that were obtained for montmorillonite, chitosan, and the biopolymer clay nanocomposite prepared from 1% montmorillonite and chitosan, in the 4,000 - 450 cm^{-1} wavenumber range. The band at 3,446 cm^{-1} , 1,638 cm^{-1} , 1,042 cm^{-1} , 791 cm^{-1} , 466 cm^{-1} corresponding to the vibration bands of the silicate and the vibration band (Al-O) at 921 cm^{-1} remain unaffected in the nanocomposite. The other bands of the nanocomposite at 2,923 cm^{-1} , 1,324 cm^{-1} are consistent with those observed in the film of pure chitosan, while the vibration bands at 3,443 cm^{-1} , 1,575 cm^{-1} , 1,042 cm^{-1} in the starting chitosan is overlapped with the bands of the silicate. The vibration band at 1,560 cm^{-1} corresponding to

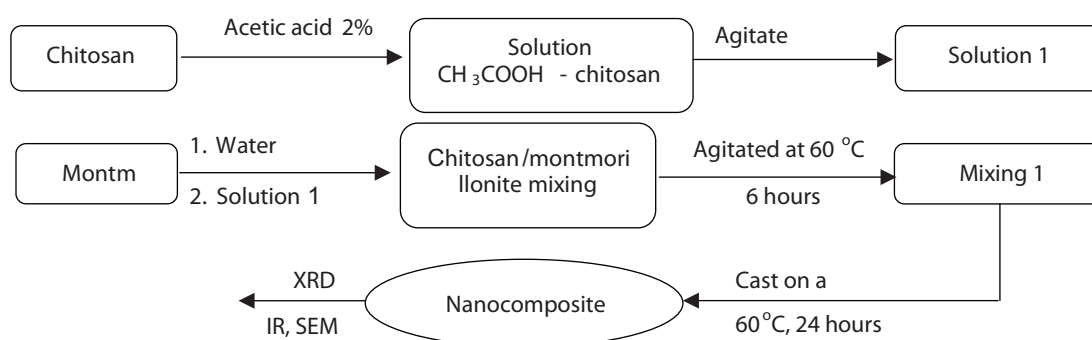
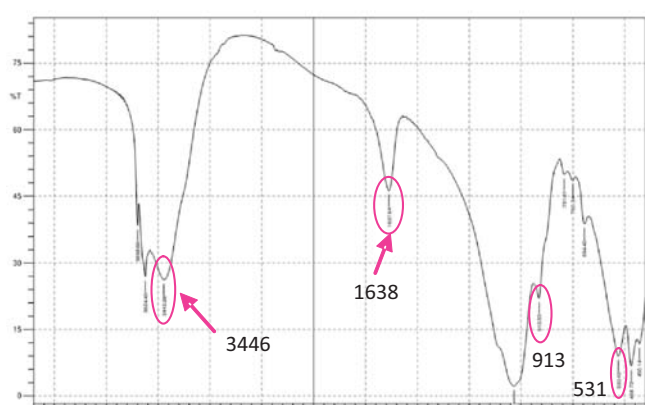
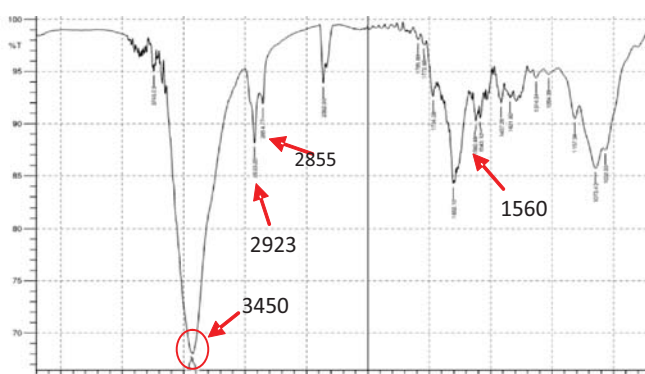


Fig.1. Procedure of synthesis material from chitosan and montmorillonite

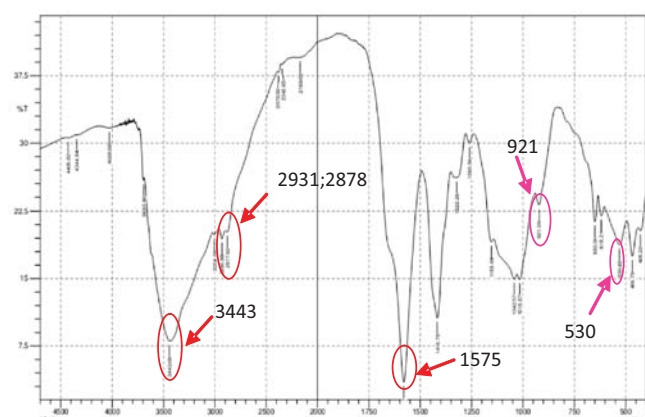
the deformation vibration of the protonated amine group in the chitosan film is shifted toward stronger frequency values $1,575\text{cm}^{-1}$ in the nanocomposite, indicating the electrostatic interaction between such groups and the negatively charged sites in the clay structure. Besides, the bands attributed to the intercalated chitosan (C-H stretching on methyl ($2,931\text{cm}^{-1}$) and methylene ($2,878\text{cm}^{-1}$) groups) are observed in the spectra of the nanocomposite [10].



(a)



(b)



(c)

Fig.2. IR spectra of montmorillonite (a), chitosan (b), the nanocomposite chitosan/montmorillonite 1% (c)

3.2. X-ray diffraction analysis of nanocomposites

The nanocomposite was analysed by XRD and the power patterns of montmorillonite are presented in Fig.3. A typical diffraction peak of montmorillonite is 6.94° , responding to a basal spacing of $14.87\text{\AA}$. After intercalation with chitosan, this peak disappears. The movement of the typical diffraction peak of montmorillonite to lower angle (3°) indicates the formation of the flocculated-intercalated nanostructure. It is reported that the formation of flocculated structure in chitosan/montmorillonite nanocomposites is due to the hydroxylated edge-edge interaction of the silicate layers [11]. The intensity of the peak decreases and even disappears, indicating the formation of an intercalated-exfoliated structure in chitosan/montmorillonite nanocomposites. According to the results of XRD and FTIR, it can be concluded that almost all chitosan were intercalated into the montmorillonite interlayer and destroyed the crystalline structure of montmorillonite.

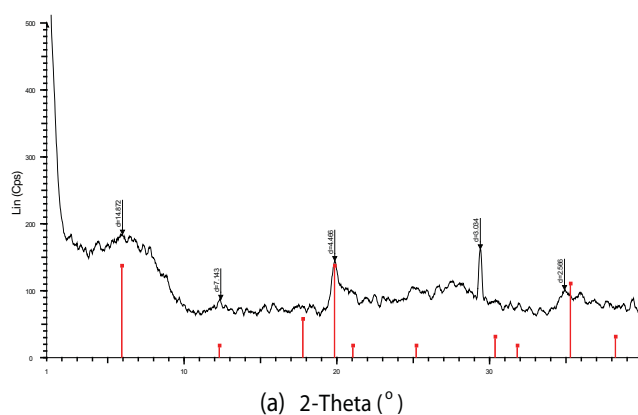
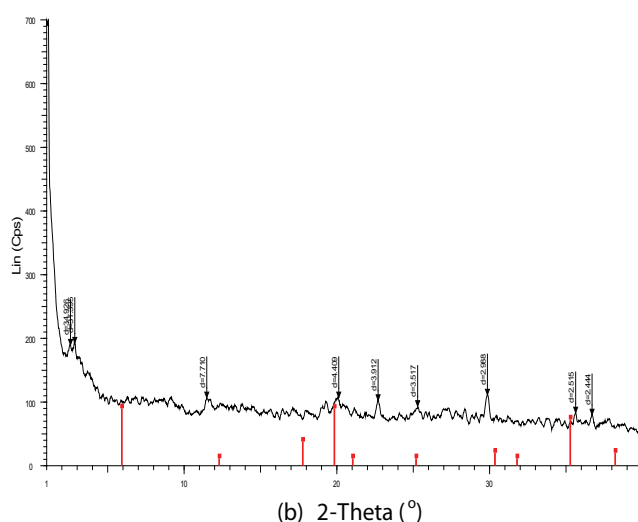
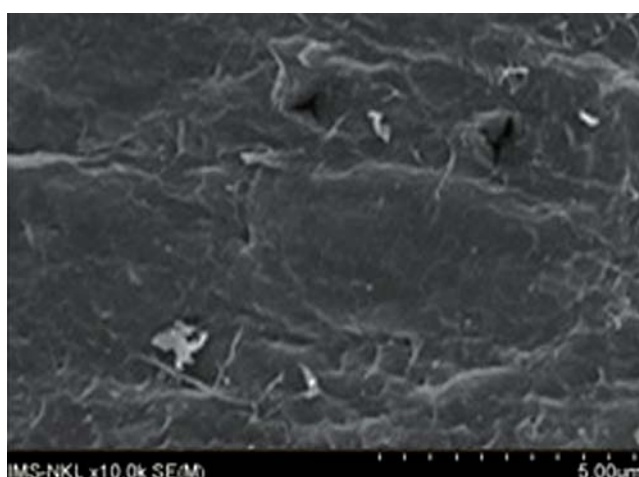
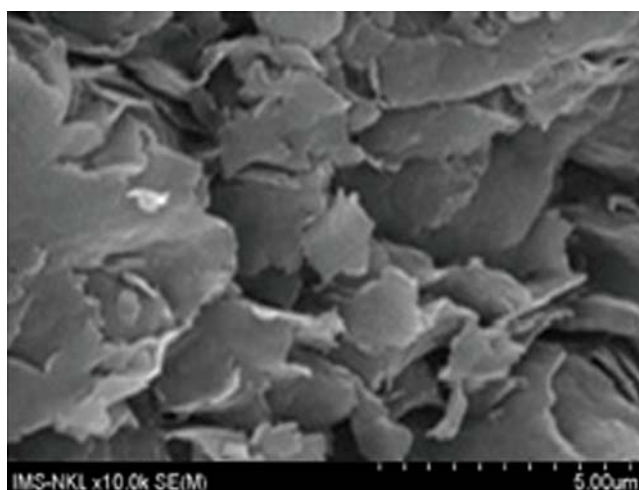

 (a) 2-Theta ($^\circ$)

 (b) 2-Theta ($^\circ$)

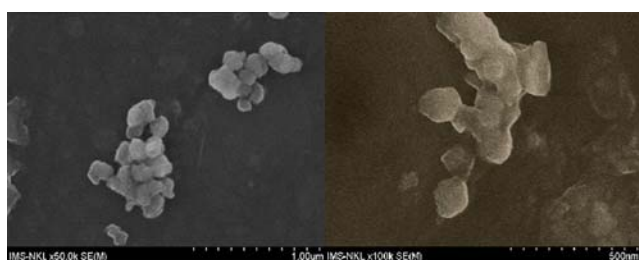
Fig.3. XRD power patterns of the montmorillonite (a), the nanocomposite chitosan/montmorillonite 1% (b)



(a)



(b)



(c)

Fig.4. SEM image of chitosan (a); SEM image of montmorillonite (b); SEM image of chitosan/montmorillonite 1% nanocomposite (c)

3.3. Scanning electron microscope (SEM) of materials

In the SEM image (Fig.4c) stacked flakes (stacks of multilayers of montmorillonite) and flocculated fraction of montmorillonite were observed. The nanocomposite clearly shows intercalated morphology with strong flocculation. Some stacks of montmorillonite multilayers appears. This result is consistent with the conclusion of XRD. The formation of a flocculated structure in the

nanocomposite is due to the hydroxylated edge-edge interaction of the silicate layers because of the hydrogen-bonding interaction between the silicate hydroxylated edge groups and the amino or hydroxyl functional groups in chitosan chains.

Table 1. Adsorption of Cu^{2+} ion at different concentration.

Adsorption experiments-sample dose 0.3g/100mL; pH 6; temperature 25°C; equilibrium time 120min.

C_o (mg/l)	10	50	75	100	120	150
C_e (mg/l)	0.54	5.68	16.36	36.31	53.45	53.55
q_e (mg/g)	3.15	14.77	19.55	21.23	22.18	22.05
C_e/q_e	0.17	0.38	0.84	1.71	2.41	2.42

Table 2. Adsorption of Cd^{2+} ion at different concentration.

Adsorption experiments-sample dose 0.3g/100mL; pH 6; temperature 25°C; equilibrium time 120 min.

C_o (mg/l)	10	50	75	100	120
C_e (mg/l)	0.10	0.84	2.44	6.66	16.44
q_e (mg/g)	3.30	16.38	24.19	31.11	34.52
C_e/q_e	0.03	0.051	0.10	0.214	0.476

3.4. Adsorption isotherms

Tables 1 and 2 show the adsorption capacity of the nanocomposite at different heavy metal ions concentrations and 25°C for samples. The adsorption capacity of the nanocomposite increases corresponding to level the metal ions concentration.

It can be seen from tables 1 and 2 that the sharp increase in adsorption capacity from 75 to 120mg/L and 50 to 100mg/L for Cu^{2+} and Cd^{2+} , respectively. However, only a slight increase in the adsorption capacity of the nanocomposite can be observed with further increase of the initial concentration of metal ions.

The adsorption process can be generally expressed by two isotherm equations, namely, the Langmuir and the Freundlich equations [12], which are represented by the following equations, respectively:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$

$$q_e = K_f C_e^{1/n}$$

Where q_m (mg/g) and b (L/mg) are Langmuir isotherm coefficients. The value of q_m represents the maximum adsorption capacity. K_f (mg/g) and n are Freundlich constants. The linear plot of C_e/q_e versus C_e is drawn for the Langmuir model of the adsorption of Cu^{2+} (Fig.5), and Cd^{2+} (Fig.6).

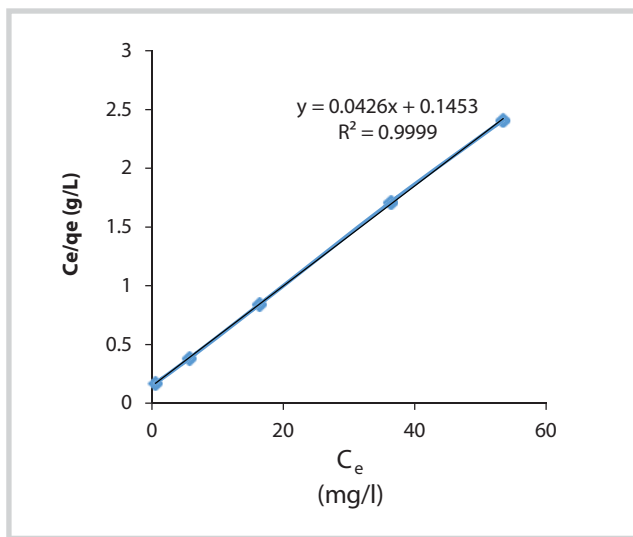


Fig.5. Langmuir plot for the adsorption of Cu^{2+} ion by the nanocomposite

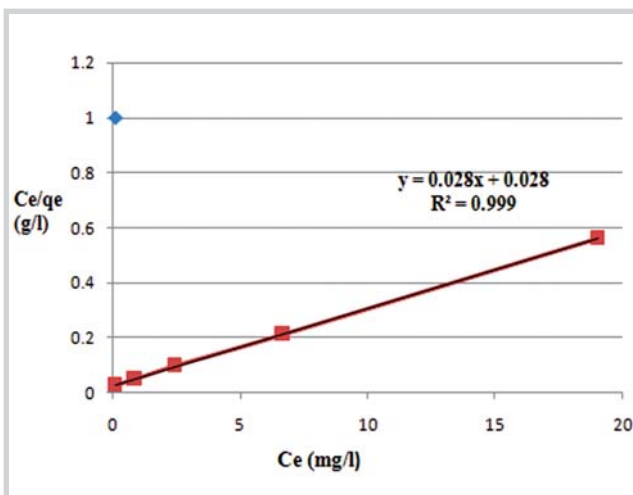


Fig.6. Langmuir plot for the adsorption of Cd^{2+} ion by the nanocomposite

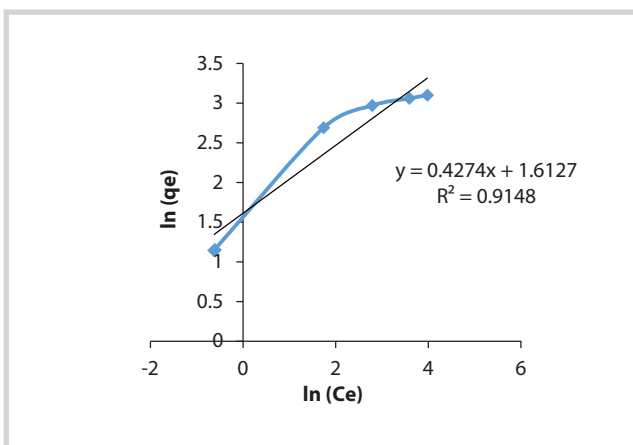


Fig.7. Freundlich plot for the adsorption of Cu^{2+} ion by the nanocomposite

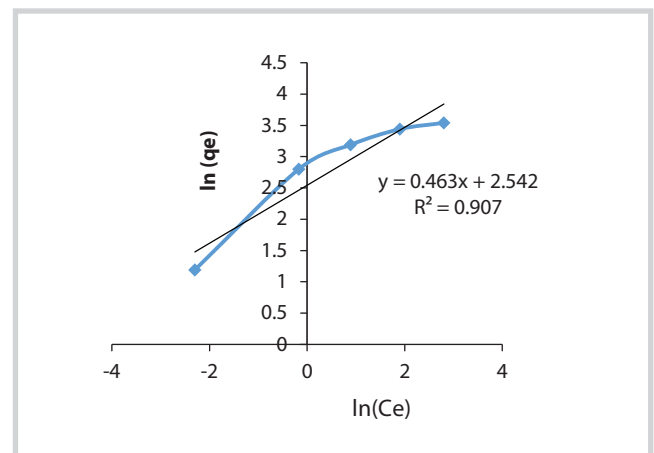


Fig.8. Freundlich plot for the adsorption of Cd^{2+} by the nanocomposite

The applicability of Langmuir isotherm suggests the monolayer coverage of the ions on the surface of nanocomposite. The linearisation of the equation and the values of R^2 for Cu^{2+} and Cd^{2+} are 0.9999; 0.999, respectively. The q_m values for the adsorption of Cu^{2+} and Cd^{2+} are 23.81 and 35.71 mg/g, respectively. The q_m value for the adsorption of Cu^{2+} by waste banana pith is 20.29 mg/g [13]. So, the chitosan/montmorillonite nanocomposite can be used as an alternative-adsorbing agent in heavy metal ions wastewaters. Figs 7 and 8 show that the values R^2 of Freundlich model for Cu^{2+} and Cd^{2+} are 0.9148 and 0.907.

Therefore, the adsorption of Cu^{2+} and Cd^{2+} on the chitosan/montmorillonite nanocomposite do not follow the Freundlich isotherm.

3.5. Adsorption kinetics

Two simplified kinetic models including pseudo-first-order and pseudo-second-order equations are analysed. A simple kinetic model that describes the process of adsorption is the pseudo-first-order equation. It was suggested by Lagergren [14] for the adsorption of solid/liquid systems and its formula is given as

$$\frac{dq_e}{dt} = k_1(q_e - q_t) \quad (1)$$

Where k_1 is the pseudo-first-order rate constant (min^{-1}), q_e and q_t are the amounts of metal ions adsorbed (mg/g) at equilibrium and at time t (min.). After integration with the initial condition $q_t = 0$ at $t = 0$, Eq. (1) can be obtained:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

Pseudo-second-order model is based on adsorption equilibrium capacity and it can be expressed as [15]:

$$\frac{dq_e}{dt} = k_2(q_e - q_t)^2$$

When the initial condition is $q_t = 0$ at $t = 0$, integration leads to Eq. (3)

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (3)$$

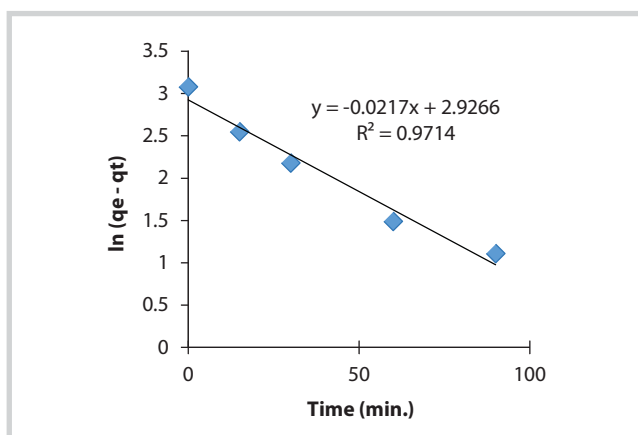


Fig.9. Pseudo-first-order model for the adsorption of Cu^{2+} ion by chitosan/montmorillonite nanocomposite

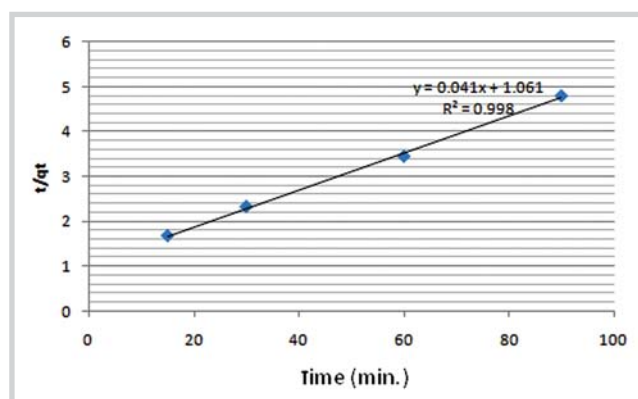


Fig.10. Pseudo-second-order model for the adsorption of Cu^{2+} ion by chitosan/montmorillonite nanocomposite

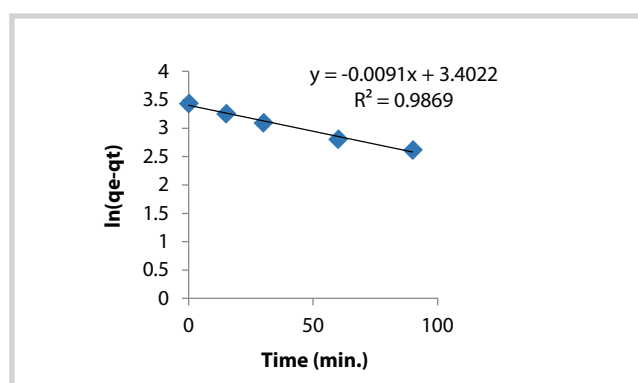


Fig.11. Pseudo-first-order model for the adsorption of Cd^{2+} ion by chitosan/montmorillonite nanocomposite

Where k_2 (g/mg.min) is the rate constant of the pseudo-second-order adsorption. The linear plots of $\log(q_e - q_t)$ versus t and (t/q_t) versus t are drawn for the pseudo-first-order and the pseudo-second-order models, respectively. The rate constants k_1 and k_2 can be obtained from the plot of experimental data. Figs.9 and 10 show the pseudo-first-order and pseudo-second-order models for the adsorption of Cu^{2+} by chitosan/montmorillonite nanocomposite.

Figs.11 and 12 show the pseudo-first-order and pseudo-second-order models for the adsorption of Cd^{2+} by chitosan/montmorillonite nanocomposite.

As seen from the Figs above, the correlation coefficients (R) of the pseudo-first-order model are 0.9714 and 0.9869 for Cu^{2+} and Cd^{2+} , respectively. For the pseudo-second-order, the correlation coefficients (R) are 0.998 and 0.993 for Cu^{2+} and Cd^{2+} , respectively.

Therefore, the adsorption of Cu^{2+} and Cd^{2+} on chitosan/montmorillonite nanocomposite are better described by the pseudo-second-order than by the pseudo-first-order. This result also indicates that the adsorption rate of metal ions depends on the concentration of metal ions at the absorbent surface at equilibrium.

4. Conclusions

The chitosan/montmorillonite nanocomposites were prepared from chitosan and montmorillonite. The results show that the relationship between adsorbing capacity (q_e) and equilibrium mass concentration (C_e) is in accordance with the isothermal adsorption equation of Langmuir. Two kinetic models, including the pseudo-first-order and pseudo-second-order, were used to analyse the heavy metal ions adsorption process. The pseudo-second-order chemical reaction kinetics provide the best correlation of the experimental data, therefore the

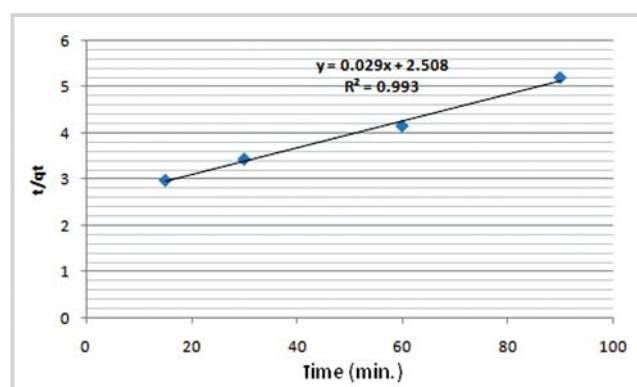


Fig.12. Pseudo-second-order model for the adsorption of Cd^{2+} ion by chitosan/montmorillonite nanocomposite

adsorption dynamics follow the laws of pseudo-second-order kinetics. The nanocomposite can thus be effectively used as an adsorbent for the removal of heavy metal ions from wastewaters.

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PETROVIETNAM NEWS

Vietnam, US co-operation in the field of oil and gas



President Truong Tan Sang and ExxonMobil's leaders. Photo: VNA

On 22 May 2014, President Truong Tan Sang received a delegation of ExxonMobil Corporation at the Presidential Palace.

At the meeting, ExxonMobil's leaders informed the Vietnamese President of the outcomes of joint projects between the US firm and the Vietnam Oil and

Gas Group (Petrovietnam), and voiced their hope that the projects will bring about practical benefits for both sides. The American firm pledged that once co-operation agreements are signed, human resources and other assets will be mobilised to accelerate this year's collaboration programmes with its Vietnamese partner.

President Truong Tan Sang highly valued US firms' contributions to further increasing two-way trade between the two countries, and highlighted the US side's support for Vietnam's participation in the Trans-Pacific Partnership (TPP) agreement negotiations. The President affirmed that Vietnam supports co-operation activities with US businesses in the field of oil and gas. President Truong Tan Sang expressed his hope that investors from the US and other countries will prosper from their investment in Vietnam, and suggested that ExxonMobil and Petrovietnam focus on realising trade deals this year.

Nguyen Hoang

PV GAS signed a MOU and framework contract with Shell to purchase liquefied natural gas (LNG)

On 16 June 2014, the Petrovietnam Gas Corporation (PV GAS) and Shell signed a memorandum of understanding (MOU) on development of Son My LNG import terminal project (Binh Thuan province) and a framework contract to purchase LNG for Thi Vai LNG import terminal project (Ba Ria - Vung Tau). The signing ceremony was witnessed by Prime Minister Nguyen Tan Dung and Dutch Prime Minister Mark Rutte.

The LNG import terminals in Son My and Thi Vai are two significant projects of PV GAS in its strategy to diversify gas supply as well as to make up for gas shortages in the coming years, contributing to ensuring national energy security and national food security. The LNG import terminal project in Thi Vai has a capacity of 1 million tons/year and is scheduled to come into operation in 2017. Son My project, which has a capacity of over 3.6 million tons/year, is expected to start operation between 2019 - 2020. The framework contract for LNG sale and purchase between PV GAS and Shell is also one of the first LNG purchase deal to ensure the supply of LNG to the import terminal project in Thi Vai.

Shell is one of the largest oil companies in the world, with extensive operations from upstream, midstream to downstream. Being a pioneer in the field of LNG with 50 years of experience, Shell currently owns one of the largest



Prime Minister Nguyen Tan Dung and Dutch Prime Minister Mark Rutte witnessed the signing a MOU between PV GAS and Shell. Photo: PVN

global networks of LNG supply and a similar track record of LNG transportation capacity. Today, Shell is the world's biggest LNG shipping operator, managing and operating 43 LNG carriers, or about 12% of the world's fleet.

In addition, Shell is one of the leading companies in technology as well as in the capacity to manage, operate and develop LNG projects, particularly the floating LNG project (FLNG) named Prelude in Australia. Shell is the first company in the world to carry out a FLNG project. FLNG is Shell's latest achievement in the development of new technology in the oil and gas industry, consolidating its leading position in technology development and improvement to deliver more value.

Hong Hanh

First oil from Thang Long field



Thang Long field first oil flow arrived at FPSO PTSC Lam Son. Photo: PVEP

At 17:29 hours on 6 June 2014, Lam Son Joint Operating Company (Lam Son JOC) formally opened the TL-8P well from Thang Long field (of Blocks 01 and 02/97, Cuu Long basin) with a flow rate of approximately 2,000 barrels of oil per day. The next wells (TL-1P, 4P, 3P, 7P, and 5P) were, in turn, put into operation in the evening and at night on the same day, bringing Thang Long field's total production rate to about 8,000 barrels of oil per day.

Lam Son JOC is the investor and operator of Thang Long and Dong Do fields. The field development plan for Thang Long and Dong Do includes 2 wellhead platforms (WHP), and a floating production, storage

and offloading unit (FPSO). The launch of Thang Long and Dong Do's production is very important as they contribute to ensuring the national energy security and the completion of PVEP/Petrovietnam's oil and gas production plan for 2014.

Thang Long and Dong Do wellhead platforms, which are suitable for small fields, were safely fabricated within 18 months, within the approved budget and using nearly 100% local services. For FPSO PTSC Lam Son, exactly 24 months after PTSC took over from the withdrawing foreign contractor and signed an EPCI contract with Lam Son JOC, the FPSO was ready to receive the first oil flow. The success in putting Thang Long field into operation has opened a new direction, an optimal strategy for the development of small fields in the future. The use of local contractors has brought cost-efficiency to the investor, and through this project local contractors have been able to show their capacity to master technology, manage and implement projects, no longer being dependent on foreign contractors.

Vu Dinh

First commercial oil flow from Diamond field

On 18 May 2014, DM-4XP well in the Diamond field (Block 01 & 02, offshore Vietnam) produced the first oil with a flow rate of 3,700 barrels per day. After DM-4XP well, the next three wells (DM-1P, 2P, 3P) will soon be put into operation, expectedly bringing the total flow rate of the entire Diamond field to approximately 9,000 barrels of oil per day.

Petronas Carigali Vietnam Limited (PCVL) is the investor and operator of the Diamond field. The Petrovietnam Exploration Production Corporation (PVEP) has worked closely with the contractors to complete all the work items of the project in time and with good quality after only 16 months of execution. In particular, the discovery of M1-65 has allowed higher catches and brought the total estimated recoverable reserves to increase by 22 - 28% compared to the original forecast.

Binh Minh

PTSC M&C signs EPCI contract for Su Tu Vang Southwest with Cuu Long JOC

On 20 June 2014, Cuu Long Joint Operating Company (Cuu Long JOC) and PTSC Mechanical and Construction Limited Company (PTSC M&C) signed an EPCI contract for the Su Tu Vang Southwest project.

The Su Tu Vang Southwest project is the target of field development in offshore Block 15-1, which is invested by Cuu Long JOC. The scope of the project includes engineering, procurement, construction, transportation and installation, hook up and commissioning of the Su Tu Vang Southwest processing platform with a total weight of 2,000 tons. Upon receiving the Letter of Intent from Cuu Long JOC on 12 November 2013 requesting EPCI services for the project, PTSC M&C has expeditiously mobilised all resources to implement the project.

So far, the works of construction and offshore installation of the Su Tu Vang Southwest's jacket have been completed safely, meeting the quality requirement and schedule. The fabrication of the topside is being



Cuu Long JOC and PTSC M&C signed an EPCI contract. Photo: PTSC

speedily carried out in PTSC M&C's construction site, and its completion, load-out, transportation, and offshore installation are scheduled for September 2014. PTSC M&C has completed the engineering, procurement, construction, transportation and installation of Su Tu Vang Southwest's jacket within 106 days, making one of the records for rapid jacket fabrication in Vietnam's oil and gas industry.

Hong Van

VPI-CPSE awarded a certificate of eligibility for environmental monitoring services



Mr. Bui Cach Tuyen, Deputy Minister of Natural Resources and Environment, awarded the certificate to CPSE. Photo: VPI

At the 5th National Conference on Environmental Monitoring on 19 June 2014, the Vietnam Environment Administration (Ministry of Natural Resources and Environment) awarded certificates of eligibility for environmental monitoring services to 3 Vietnamese units. In particular, the Vietnam Petroleum Institute's Branch - the Research and Development Centre for Petroleum Safety and Environment (VPI-CPSE) is the first unit to be awarded the certificate, with serial no.

VIMCERTS 001, in accordance with the Minister of Natural Resources and Environment's Decision No.1154/QĐ-BTNMT dated 18 June 2014. Earlier, VPI-CPSE has been inspected by the Vietnam Environment Administration and appraised by the Ministry of Natural Resources and Environment's Appraisal Council in compliance with the procedures stipulated in Decree No. 27/2013/ND-CP and Circular No. 42/2013/TT-BTNMT.

Speaking at the conference, Dr. Hoang Nguyen, Deputy Director in charge of VPI-CPSE, said the award of certificates was in line with the policy of the Ministry of Natural Resources and Environment's leaders and will facilitate healthy competition among the environmental monitoring units. The quality of field monitoring and sample analysis in the labs will be tightly controlled to ensure that the real quality of the environment at the monitored area is reflected.

This certificate contributes to affirming VPI-CPSE's position and capacity in the field of environmental monitoring, especially sample taking for environmental monitoring at onshore and offshore constructions in the oil and gas industry.

Thanh Kim

Vietnam and Azerbaijan beef up energy co-operation

During a state visit to Vietnam, on 19 May 2014, Azerbaijan's President Ilham Aliyev had talks with President Truong Tan Sang and met the Party's General Secretary Nguyen Phu Trong, Prime Minister Nguyen Tan Dung, and National Assembly Chairman Nguyen Sinh Hung. The leaders focused discussion and agreement on measures to promote all aspects of Vietnam - Azerbaijan relations, especially in economic, trade and investment areas. In particular, it was proposed that Azerbaijan create favourable conditions for Petrovietnam's effective and long-term investment and co-operation in Azerbaijan.

On the same day in Hanoi, Dr. Do Van Hau, President and CEO of

Petrovietnam received the leaders of the State Oil Company of the Azerbaijan Republic (SOCAR). On behalf of the State and the Government of Vietnam, Vice Minister of Industry and Trade Tran Tuan Anh awarded the Friendship Order of the Socialist Republic of Vietnam to Mr. Khoshtakht Yusifzadeh Baghi Oglu, SOCAR's First Vice President, for his important contribution to the development in the field of oil and gas of the two countries.

Mr. Khoshtakht affirmed that he would continue to positively contribute to the consolidation and development of the excellent friendship and co-operation between Vietnam and Azerbaijan, particularly in the field of oil and gas.

Tran Huong

Signing ceremony for FPU DH-01 and calm buoy repair contract



A signing ceremony was recently held in Ho Chi Minh City for Dai Hung drilling rig and calm buoy repair contract between Petrovietnam Exploration Production Corporation POC (PVEP POC) and Dung Quat Shipbuilding Industry Company Ltd. (DQS).

Dai Hung drilling rig has a length of 108.2m, width 67.36m, and height 68.60m. This is one of the most important rig for exploration and production of PVEP-POC. Dai Hung rig is expected to arrive at Dung Quat Shipyard in early October 2014 and the repair will take about 180 days.

Quoc Thinh

PVFCCo's Petrochemical Manufacturing Facility supplies more than 5,000 drums of products to the market



PVFCCo's Petrochemical Manufacturing Facility has a production capacity of 25,000 drums/year. Photo: DPM

Petrovietnam Fertilizer and Chemical Corporation (PVFCCo) announced that its Petrochemical Manufacturing Facility in Ba Ria - Vung Tau has been officially operational since the beginning of 2014. Until now, the Facility has provided more than 5,000 drums of special petrochemical products to customers, earning about 60 billion VND in revenues. At full capacity, the Facility can generate approximately 300 billion VND in annual revenues.

The Facility has a production capacity of 25,000 drums/year, processing and manufacturing specialised chemicals, chemical products for oil and gas production,

and chemicals used in oil refineries. The Facility was built on the basis of an agreement between PVFCCo and Baker Hughes Petrolite to manufacture specialised chemicals and chemical products used in oil production and refinery in accordance with Baker Hughes' manufacturing and quality management process. Previously, these chemicals and chemical products had to be imported 100% from the United States, UK, and other European countries. This is the first specialised chemicals and chemical products facility invested by a member company of the Vietnam National Oil and Gas Group in order to supply specialised chemicals to oil and gas companies operating in Vietnam.

The construction of the Petrochemical Manufacturing Facility started in late 2013 in Dong Xuyen Industrial Park, Rach Dua Ward, Vung Tau City, Ba Ria - Vung Tau Province. The Facility has been equipped with modern machinery and equipment from Japan, Germany, and the United States, complying with strict requirements of Baker Hughes' manufacturing process for specialised chemicals and chemical products. Besides, the Facility has also been rated by Baker Hughes as meeting its standards on equipment, technology, laboratory, safety devices, fire control and environment.

Dinh Khoi

PVC-MS accelerates the procurement of materials for Thai Binh 2 Thermal Power Plant

The Petroleum Equipment Assembly & Metal Structure Joint Stock Company (PVC-MS) signed two contracts on 6 June 2014 in Hanoi with PV Engineering and Phu Dat - Vinh Da consortium of contractors for supply of materials for Thai Binh 2 Thermal Power Plant.

Accordingly, PV Engineering will supply to PVC-MS steel sheets < 40mm, worth nearly 38 billion VND, and steel sheets ≥ 40mm, worth nearly 34 billion VND. Phu Dat - Vinh Da consortium of contractors will provide shaped steels H < 500mm, worth more than 64.6 billion VND and shaped steel H ≥ 500mm, worth more than 40.3 billion VND. These contracts are a part of the tender package for "supply of materials, fabrication and installation of steel structure" for the turbine hall and the central control building of Thai Binh 2 Thermal Power Plant Project. Apart from this package, PVC-MS is assigned to perform the package of installing the turbine/generator of Unit 2 and other ancillary items.



PVC-MS signed contract with PV Engineering. Photo: PVC

PVC-MS is working closely with the contractors to accelerate the procurement of materials. It is expected that the company will carry out fabrication works in August 2014, and launch installation works in late October 2014.

Minh An



The first half-year of 2014 is a period of quasi-stable oil demand growth trend in the global markets. This trend is linked with the US and OECD economic recovery performances. However, oil price fluctuation in recent days generally depends on the risk of increased tensions in Ukraine and in the Pacific region.

The West Texas Intermediate (WTI) for delivery in July was down 21 UScents to 103.37USD a barrel after rallying 86 UScents in New York on 29 May, but at the same time Brent North Sea crude for July gained 4 UScents to 110.01 a barrel in morning trade. According to the US Department of Energy, overall US inventories are rising,

but gasoline supplies are falling in early June and this decline in gasoline supplies is attributed to the summer driving season in America.

In Europe, the oil price rising is due to the uncertainty of the Russia's gas export linked with the escalating fighting between government troops and East - Ukraine separatist partisans. Investors fear the conflict will disrupt supplies and send energy prices soaring at month's end.

For 2014, world demand could increase by 1.4 million barrels/day and oil supply outside the OPEC could increase by 1.6 million barrels/day. These estimates suggest that the supply - demand balance in 2014 would be similar to that in 2013 and OPEC could be able to manage the market. The future price of crude oil depends on this future balance.

The state of the world economy directly affects the demand for energy and for oil.

Table 1. Oil & gas prices in 2014 third quarter contracts

Commodity	Units	Price	Change	% change	Contract
Crude oil WTI	USD/barrel	102.71	-0.87	-0.84%	July 2014
Brent	USD/barrel	109.41	-0.56	-0.51%	July 2014
TOCOM crude oil	JPY/kL	65,950	-250.00	-0.38%	October 2014
Nymex natural gas	USD/million Btu	4.54	-0.02	-0.37%	July 2014
RBOB gasoline	USD/gallon	299.80	+0.15	+0.05%	July 2014
Nymex heating oil	USD/gallon	288.82	-3.17	-1.09%	July 2014
ICE gasoil	USD/million tons	893.75	-12.50	-1.38%	July 2014
TOCOM kerosene	JPY/kL	80,420	-290.00	-0.36%	December 2014

Sources: www.bloomberg.com

Table 2. Oil prices from big global suppliers in second quarter of 2014 (USD/Bbl)

	14 April 2014	May 2014	June 2014 (estimated)
OPEC reference basket	105.44	105.44	108.49
Arab light - Saudi Arabia	105.80	103.50	109.06
Basrah light - Iraq	103.16	101.08	107.03
Bonny light 37° - Nigeria	112.22	107.70	111.78
Es Sider - Libya	109.42	108.70	112.71
Girasol - Angola	110.21	105.06	111.82
Iran heavy - Iran	105.40	104.50	108.04
Kuwait export - Kuwait	104.21	101.05	107.48
Marine - Qatar	105.44	104.08	107.65
Meruy - Venezuela	96.06	93.37	98.96
Murban - UAE	108.35	103.52	110.19
Oriente - Ecuador	95.47	93.25	99.13
Saharan blend 44° - Algeria	110.36	106.50	112.89
Minas 34° - Indonesia	107.22	101.52	106.52
Fateh 32° - Dubai	105.55	101.34	107.80
Isthmus 33° - Mexico	102.59	104.05	110.10
Tia Juana light 31° - Venezuela	109.67	112.38	116.00
Brent 38° - UK	107.84	108.00	112.78
Urals - Russia	108.06	107.03	111.77

Sources: *Oil & Gas Journal* 23 June 2014, www.oil-prices.net

Table 3. Worldwide crude oil and gas production in first 2 months of 2014

	Crude oil, 1,000 b/d		Gas, bcf	
	Feb.	Jan.	Feb.	Jan.
Argentina	538	539	91.3	101.6
Bolivia	48	48	63.0	63.0
Brazil	2,150	2,140	63.4	68.4
Canada	3,500	3,484	397.0	395.0
Colombia	1,010	1,020	30.0	30.0
Ecuador	520	530	1.0	1.0
Mexico	2,501	2,506	183.3	200.3
Peru	165	170	34.5	36.7
Trinidad	82	75	123.1	124.2
United States	8,033	8,005	2,004.0	2,215.5
Venezuela	2,420	2,460	60.0	60.0
Other Latin America	89	89	4.0	4.0
Western Hemisphere	21,056	21,066	3,054.6	3,299.7
Austria	17	17	4.0	4.0
Denmark	168	161	11.1	13.8
France	15	15	0.1	0.1
Germany	49	33	28.0	28.0
Italy	106	100	24.0	24.0
Netherlands	25	23	120.0	120.0
Norway	1,621	1,633	328.4	349.6
Turkey	45	45	1.5	1.5
United Kingdom	921	845	105.3	115.0
Other Western Europe	9	9	2.3	2.3
Western Europe	2,976	2,881	624.7	658.3
Azerbaijan	987	844	67.1	95.3
Croatia	11	11	4.5	4.5
Hungary	12	12	6.0	6.0
Kazakhstan	1,610	1,642	116.5	130.7
Romania	81	81	20.0	20.0
Russia	10,542	10,506	2,058.8	2,327.2
Other FSU	396	375	490.9	568.6
Other Eastern Europe	51	52	20.9	20.9
Eastern Europe and FSU	13,690	13,523	2,784.7	3,173.2
Algeria	1,100	1,080	230.0	230.0
Angola	1,610	1,650	4.0	4.0
Cameroon	61	61	2.0	2.0
Congo (former Zaire)	28	28	-	-

	Crude oil, 1,000 b/d		Gas, bcf	
	Feb.	Jan.	Feb.	Jan.
Congo (Brazzaville)	290	290	-	-
Egypt	680	680	105.0	105.0
Equatorial Guinea	255	255	0.1	0.1
Gabon	260	260	0.3	0.3
Libya	360	500	25.0	25.0
Nigeria	1,980	1,920	70.0	70.0
Sudan	470	470	-	-
Tunisia	58	58	9.0	9.0
Other Africa	315	315	9.1	9.1
Africa	7,467	7,567	454.5	454.5
Bahrain	49	49	32.0	32.0
Iran	2,850	2,780	465.0	465.0
Iraq	3,600	3,090	28.0	28.0
Kuwait	2,780	2,780	40.0	40.0
Oman	951	959	94.0	94.0
Qatar	700	720	350.0	350.0
Saudi Arabia	9,850	9,760	250.0	250.0
Syria	30	30	14.0	14.0
United Arab Emirates	2,740	2,720	165.0	165.0
Yemen	150	130	-	-
Other Middle East	1	1	19.7	22.1
Middle East	23,701	23,019	1,457.7	1,460.1
Australia	355	328	140.0	154.9
Brunei	131	119	35.7	36.5
China	4,214	4,152	381.0	402.2
India	779	783	97.4	108.5
Indonesia	800	787	202.0	202.0
Japan	16	13	9.8	10.4
Malaysia	507	500	183.7	203.6
New Zealand	36	40	13.0	13.7
Pakistan	86	87	114.4	127.9
Papua New Guinea	30	30	0.5	0.5
Thailand	233	225	118.9	130.4
Other Pacific	28	28	109.3	111.5
Asia Pacific	7,875	7,752	1,469.7	1,566.1
Total world	76,435	75,478	9,813.9	10,579.9
OPEC	30,510	29,990	1,688.0	1,688.0

Sources: Oil & Gas Journal, 12 May 2014

Any improvement in economic performance will soon be reflected as an increase in demand for oil. Conversely, a recession will soon be reflected as a decrease in demand for oil. Hence, the important factors for the future of the oil market are how quickly the industrialised countries come out of recession and how fast their economies grow. But oil demand of these countries is not expected to grow that much; for some could decline in the coming years. Therefore, the more critical factor would be the economic performance of the developing countries and the rest of the world because the future growth of world oil demand will be in these countries.

Public policy, such as mandatory speed limits, standards and specifications for the efficient use of energy and oil, mandatory substitution of oil by other energies, government subsidies, etc... are also other factors which

significantly influence the demand.

Environmental issues in all countries increasingly direct public policy aimed at reducing the consumption of oil, though most of these policies will have a medium to long-term impact.

Oil intensity fell about 50% for industrialised countries between 1979 and 2007. A similar trend is observed for the developing and emerging economies but it is not very clear. The oil intensity of GDP of these countries remained high during their economic development phase but stabilised and has been declining since the 1990s.

Global gas supply outlook

BP's Energy Outlook 2030 forecasts that global gas supply will reach 459 billion ft³/day (4,7 trillion m³/year) by

2030, representing an annual growth rate of 2%, the fastest of any fossil fuel.

BP says shale gas will feature heavily, accounting for 37% of overall gas supply growth over the period. But the greatest increment in conventional gas production in the developing world is a lot bigger than that seen in shale gas. The conventional non-OECD supply will come from the Middle East, set to add 31 billion ft³/day over the period, with developments in Africa - such as the clutch of prospective LNG export projects off East Africa-adding 15 billion ft³/day, BP reckons.

Most of the shale gas growth will be in North America, primarily the US, but with Canada and Mexico also making significant contributions. North America will account for 54 billion ft³/day of the 74 billion ft³/day global shale gas output in 2030. Outside North America, China will be the most successful shale gas developer - going from essentially nothing now to around 6 billion ft³/day in 2030. By contrast, the EU will be producing just 2.4 billion ft³/day. There are some obstacles to significant development in Europe, including environmental and political objections, legal bans in some countries on hydraulic fracturing, and lack of service sector capacity. In North America, BP reckons burgeoning shale gas supplies will tip the region - initially just the US - into becoming a net exporter of gas in the form of LNG by 2017. Overall, BP expects North American LNG exports to reach 8 billion ft³/day by 2030, equivalent to around 61 million tons/year. This estimate puts BP at the higher end of recent projections for North American LNG export capacity, but is actually just a quarter or roughly 32 billion ft³/day of the total notional capacity that US project developers alone have submitted for government approval. BP sees notional North American LNG export volumes dictated instead both by available gas output and by the consequent narrowing in the spread between cheap domestic gas and international prices, which would render some projects uneconomic.

Australia

Analysts reckon the Australian onshore greenfield development would cost about 40 billion USD. Santos says its 7.8 million tons/year Gladstone LNG remains on

Table 4. Australian LNG Projects 2014 - 2020

Unit: Million tons/year

Project	2014	2015	2016	2017	2018	2019	2020
North West Shell	16.3	16.3	16.3	16.3	16.3	16.3	16.3
Darwin	3.6	3.6	3.6	3.6	3.6	3.6	3.6
Pluto	4.3	4.3	4.3	8.6	12.9	12.9	12.9
Gorgon	-	15.6	15.6	20.0	20.0	20.0	20.0
Queensland Curtis LNG	8.5	8.5	8.5	8.5	8.5	8.5	8.5
Australia Pacific LNG	-	4.5	9.0	9.0	9.0	9.0	9.0
Fisherman's Landing	-	1.9	3.8	3.8	3.8	3.8	3.8
Wheatstone	-	-	8.6	8.6	8.6	8.6	8.6
Ichthys	-	-	8.4	8.4	8.4	8.4	8.4
Prelude	-	-	-	3.6	3.6	3.6	3.6
Sunrise	-	-	-	4.0	4.0	4.0	4.0
Browse	-	-	-	12.0	12.0	12.0	12.0
Arrow LNG	-	-	-	4.0	8.0	8.0	8.0
Bonaparte	-	-	-	2.0	2.0	2.0	2.0
Gladstone LNG	7.8	7.8	7.8	7.8	7.8	7.8	7.8
Total	40.5	62.5	85.9	120.2	128.5	128.5	128.5

Sources: Oil & Gas Journal, 5 May 2014

track for first production in 2015, while the 6.9 million tons/year ExxonMobil-operated PNG LNG plant in Papua New Guinea, in which it owns 13.5%, starts up in 2014.

Based on projects now in operation and those committed or under construction, Australia's LNG exports are forecast to increase from about 20 million tons/year now to more than 63 million tons annually by 2016 - 2017, which would make it the world's biggest LNG exporter after Qatar (Table 3). But the industry is being rocked by delays and budget blowouts that have made Australian schemes the most expensive in the world.

India's LNG construction

In 2013, Gail India commissioned India's third LNG import terminal, with a nameplate capacity of 5 million tons/year, at Dabhol in the western state of Maharashtra, Janvar. Three days later, Petronet LNG, the country's biggest importer of the super-cooled fuel, said it will open the country's fourth terminal at Kochi, in the south in the second quarter of 2013, adding to its Dahej terminal in Gujarat.

About half a dozen more companies, including France's GDF and Royal Dutch Shell - which already operates the Hazira terminal in the Western state of Gujarat - are also scrambling to add new terminals, while others like BP and Japan's Mitsui are considering boosting Indian regasification capacity, which the government last year forecast would expand four-fold to 50 million tons/year by March 2017 from 13.6 million tons at the

end of 2012. Key suppliers such as Qatar Petroleum are meanwhile trying to gain a foothold by mulling purchases of stakes in existing players.

The frenzy is being driven by long-term forecasts that gas demand in Asia's third-largest economy will continue to outstrip domestic production on growing consumption by refineries, and power and petrochemicals plants. Analysts at Jefferies & Co said in November they reckon domestic output will likely average 90 million - 103 million m³/day (3.2 - 3.6 billion ft³/day) until March 2015. Gas demand is forecast to rise to 473 million m³/day by March 2017 from 293 million m³/day in March 2013. With no new major supply coming on stream until 2017, at the earliest, gas shortages will increase. These are already crippling growth in fertiliser output, and leading to chronic power shortages.

In the medium term, LNG is seen as the most likely way of bridging the supply-demand gap. India's import will rise to 77 million m³/day (about 21 million tons/year of LNG) by March 2015, as the government moves to ease existing bottle-necks that include lack of regasification capacity and pipeline infrastructure, as well as low domestic prices that make imports uneconomic.

Domestic output has been falling for the past 24 months. Analysts say the problem stems from lack of exploration spending because of the government policy of keeping gas prices artificially low to help power and fertiliser plants, which have to sell their output at subsidised rates.

Gas prices vary from 4.20 - 5.70USD/million Btu while spot LNG prices have been as high as 17USD/million Btu.

Oil Minister Veerappa Moily said that India needs to step up gas use as it is a relatively clean fuel. India hopes to increase its current share from 9% in its primary energy basket to the current global average of 23%. New Delhi also plans to focus on unconventional sources like shale gas and expects soon to introduce a policy on domestic shale exploration.

India is also studying pipeline imports, with the proposed Turkmenistan - Afghanistan - Pakistan - India project potentially supplying 38 million m³/day by 2018. But analysts are dubious, given political instability in transit countries.

With dependence on LNG set to grow, importers are rushing to tie up supplies by acquiring stakes in proposed

export projects in East Africa, and through long- and medium- term purchase agreements.

In the past 13 months, Gail has nailed down 6 million tons/year starting in April 2017, including 3.5 million tons/year from Cheniere Energy's Sabine Pass, the only proposed US export project with approval to supply to countries without free trade agreements with the US like India. Petronet has also said it is seeking long-term deals.

Algeria

Algeria is the third largest gas supplier to Europe and a significant LNG exporter in the world with a capacity of 9 billion m³/year (870 million m³/day) of gas and 60,000 barrels/day of condensate. Deliveries to Italy via the Transmed are usually 70 - 75 million m³/day and to Spain via the Medgas and Maghreb - Europe pipelines are unaffected by global economic crises, and the long-term ramification of Algerian petroleum could be huge. The economy of Algeria remains heavily skewed toward hydrocarbons, which account for roughly 45% of GDP, 98% of exports and up to two-thirds of state revenue, so security measures for the infrastructure of Algerian petroleum industry are vital.

In 2013, Algeria's parliament had amended hydrocarbons legislation to focus taxes more on company profits than turnover, and cancel an unpopular windfall profits tax, while the government is preparing to launch new licensing round focused on unconventional resources. The giant Hassi R'Mel gas field in the Northern part of the country remains the centrepiece of gas export infrastructure, but is set to decline by the 2020s, potentially jeopardising Algeria's role as gas exporter unless the drop can be offset by tight gas and shale gas.

Lack of infrastructure and red tape are already holding up major gas projects in the southwest, and the threat of terrorism and higher security costs must now be added to the problems. The GR5 pipeline designed to link Southwestern fields to Hassi R'Mel, finally got the go-ahead last October and should be operational by November 2015.

Algeria is also making little headway in the booming Asian LNG market, prompting a growing realisation within Sonatrach that it may have to soften on oil-linked gas pricing to incorporate an element

of spot indexation to secure Asian buyers. In 2011 Algeria sold 200,000 tons of LNG across Asia, out of total exports of 12.5 million tons. Around 12.2 million tons went to Europe, where gas demand continues to decline. But with global competition set to increase over the next few years as new LNG export schemes come on line in Australia, the US, and potentially East Africa and the Eastern Mediterranean, Sonatrach needs to up its game. A new export plant at Skidda is due on stream this year and another at Arzew by 2015 with a combined capacity of 10,000,000 tons/year that should theoretically hoist Algeria's name plate capacity to 60 million tons/year. But Algiers will likely have to close some older facilities, given that its LNG sales are less than one-quarter of that volume and no LNG contracts are yet linked to the new capacity.

Azerbaijan gas export

Azerbaijan's campaign to become a major gas exporter to Europe, cutting into sales from its giant Russian neighbour, is underpinned by the knowledge that new Caspian discoveries will augment supplies from its massive Shaz Deniz field which has reserves of 1.2 trillion m³ of gas and 240 million tons of condensate for years to

come. But it is still far from clear how much extra gas these fields will produce and how long it will take to bring them on stream.

Deliveries from Shaz Deniz Phase 2 to Europe via a new southern corridor across Turkey are due to kick off in 2017, with 10 million m³/year earmarked for EU customers and 6 billion m³/year for Turkey. According to Gulmira Rzaeva, energy security researcher at Baku's Centre for Strategic Studies of the President of Azerbaijan, Baku hopes to double gas exports to the EU to 20 billion m³/year by 2020 - 2025 - although that pales in comparison with Russian exports to Europe of 112.7 billion m³ in 2012.

BP, Chevron, Total, RWE Dea (Germany) are the dominant overseas players in Azerbaijan, which operates their blocks with state oil company Socar. Azerbaijan is planning a 14 billion USD gas, oil and petrochemicals complex near the capital Baku that will include a gas-processing plant with a design capacity of up to 15 billion m³/year. The complex, producing ethylene, propylene, and polyethylene, is not expected to start up before 2020.

Ha Phong (introduction)



PROFESSIONAL MASTER PROGRAMME IN GEO-EXPLORATION & PETROLEUM GEO-ENGINEERING

The Asian Institute of Technology (AIT), in co-operation with the Vietnam Petroleum Institute (VPI), is now offering the Professional Master Programme in Geo-Exploration and Petroleum Geo-Engineering (GEPG).

❖ Practical curriculum offered with flexibility to suit participants' schedule

❖ Overseas internship and research

❖ Work with experienced VPI experts at an outstanding research facility with PVT, Cores, Geochemistry, Petrography, Lithology and Biostratigraphy laboratories system

❖ Renowned lecturers from institutes/universities around the world e.g. Oklahoma (USA), Chulalongkorn (Thailand), Kyoto University (Japan), Schlumberger, Hanoi University of Mining and Geology, etc.

Since its launch in 2008 in Ho Chi Minh City - Vietnam, 5 GEPG courses have been successfully organised to date and attracted enthusiastic participants from many oil and gas companies

in Vietnam such as PVEP, Cuu Long JOC, Lam Son JOC, Con Son JOC, Thang Long Truong Son JOC, Chevron, Hoang Long - Hoan Vu JOCs, Pearl Oil, Phu Quy POC, Schlumberger, PV Drilling & Baker Hughes, Rosneft, Fairfield, Nippon Oil and Salamander Energy, etc. With a practical study programme focusing on exploration and production, experienced lecturers and state-of-the-art study facilities, GEPG has always received positive evaluation from its graduates. We are pleased to announce that the GEPG programme will be held at VPI's head office - 173 Trung Kinh Street, Yen Hoa Ward, Cau Giay District, Ha Noi.

The Vietnam Petroleum Institute (VPI) - the leading science research & development subsidiary of PetroVietnam, reputed for high quality training course provider - and the Asian Institute of Technology - the premier international postgraduate institution of engineering and management - believe that knowledge and skills improvement are the key to achieve development goals and success.

STRUCTURE AND DELIVERY

PME-GEPG programme	Course work		Internship/Research	Graduation
	1 st semester	2 nd semester	Inter-semester	
Location	AIT Vietnam VPI	AIT Vietnam VPI	Southeast Asia	AIT
Program (credit)	12 crd Course work	12 crd Course work	9 crd internship/research	

Note: The course is offered in English with a minimum length of 1 year

CURRICULUM

Semester	Time	Content	Duration
1 st	August - December	Fundamentals of Geo-exploration	12 crd
		Petroleum reservoir engineering	
		Drilling and well completion operation	
		Decision analysis & risk management in oil and gas industry	
2 nd	January - May	Exploration geophysics	12 crd
		Petrophysics	
		Petroleum production Engineering	
		Petroleum geochemistry	
Inter-semester	June - December	Practical lab session at VPI Internship/Research	9 crd

Note: Flexible schedule, graduation in December

For more information about our Programme, please visit our website www.vpi.pvn.vn or contact our address as below:
Vietnam Petroleum Institute - Centre for Petroleum Training and Information (CPTI)
14th floor, 173 Trung Kinh St, Yen Hoa Ward, Cau Giay Dist., Ha Noi
Tel: 84-4-37843061/Ext: 1444; Fax: 84-4-37844156, Email: cpti@vpi.pvn.vn.

TENTATIVE TRAINING COURSES AT VIETNAM PETROLEUM INSTITUTE IN 2014

No	Course	Code	Tentative time	Venue
A	DOCTORATE TRAINING PROGRAMME			
	<i>Major: PETROLEUM ENGINEERING</i>	62 52 06 04	3 - 4 years	HN
B	SHORT-TERM TRAINING PROGRAMME			
I	Petroleum E&P field			
1	Well log interpretation and reserve calculation	EXP_4025	4 days	HN
2	Basic/Advanced training on Geology - Geophysics	EXP_1007	3 days	HN/HCM
3	Geological structure interpretation (Lang Son - Loc Binh - Mau Son field trip)	EXP_4032	5 days	HN
4	Fractures and faults analysis (Do Son - Hai Phong field trip)	EXP_4005	5 days	HN
5	Lithological facies and sedimentary environment (Cat Ba field trip)	EXP_3003	7 days	HN
6	Sequenced stratigraphy (field trip)	EXP_3001	5 days	HN
7	Hydrocarbon exploration methods	EXP_1001	5 days	HN
8	Petroleum production engineering, advanced	EXP_2009	3 days	HN
9	Hydrocarbon system and conditions for hydrocarbon accumulations in fractured basement	EXP_2012	5 days	HN
10	Seismic data interpretation, basic	EXP_2015	5 days	HN
11	Seismic data interpretation, advanced	EXP_2015	5 days	HN
12	Geochemistry for petroleum exploration, basic	EXP_1002	3 days	HN
13	Geochemistry in petroleum exploration, advanced	EXP_2010	4 days	HN
14	Flow Assurance	EXP_4030_E	5 days	HN
15	Well-Test Analysis	EXP_4031_E	5 days	HN
16	Well log interpretation, advanced	EXP_2016	5 days	HN/HCM
17	Identification of stratigraphic boundaries and reservoirs by geophysical methods	EXP_2022	5 days	HN
18	(Well log) processing and interpretation for gas - condensate bearing section	EXP_2014	5 days	HN
19	Seismic study of AVO inversion	EXP_4027	5 days	HN
20	Core Analysis/PVT Analysis	PRD_2007	2 days	HCM
21	Well log analysis and measured parameter justification in potential/reserve calculation	EXP_2025	5 days	HN/HCM
22	Seismic data interpretation in reserve calculation	EXP_2026	5 days	HN/HCM
23	Application of sequenced stratigraphy and seismic stratigraphy in hydrocarbon potential assessment	EXP_2027	5 days	HN/HCM
24	Introduction to Petrel software in Geology - Geophysics	EXP_2028	5 days	HN
II	Petrochemistry, petroleum refining and processing			
25	Petrochemical processing	DWN_1002	3 days	HCM
26	Biofuels	DWN_1005	3 days	HCM
III	Safety and environment in oil and gas			
27	Risk management in oil and gas industry	HSE_1002	3 days	HCM
28	Introduction to the legislation on safety, health and environment in oil and gas industry	HSE_1003	2 days	HN/HCM
29	Identification and management of risk in oil and gas industry	HSE_1002	3 days	HCM/HN
30	Oil spill response in petroleum operations	HSE_2003	3 days	HCM
31	Labour environment monitoring in oil and gas industry	HSE_1005	2 days	HCM
32	Control of solid and hazardous waste in oil and gas industry	HSE_1004	2 days	HCM
33	Environment monitoring techniques	HSE_1006	2 days	HN
IV	Petroleum economics and management			
34	Petroleum contracts and E&P investment project evaluation	EBA_3002	5 days	HN
35	Disputes in international petroleum contracts: Litigation skills at economic arbitration/court	EBA_3001	6 days	HN
36	Petroleum project management	EBA_1006	5 days	HN
37	Enterprise risk management	EBA_1007	5 days	HN/HCM
38	Materials/goods management	EBA_1008	4 days	HN
39	Training on fostering knowledge and professional skills to Controller and Supervisory board members	EBA_2004	5 days	HN
40	Law in foreign trade and commercial disputes settlement by arbitration	EBA_2014	6 days	HN
V	English			
41	English for petroleum industry	ENG_5002	60 hours	HN
42	English for TOEIC (450-500)	ENG_1001_I	60 hours	HN
43	English for TOEFL	ENG_2001	60 hours	HN
44	English for IELTS (5.0)	ENG_3001_I	60 hours	HN
VI	Other fields			
45	Anti-corrosion and metal protection for oil and gas constructions (basic)	MDS_1001	2 days	HN/HCM
46	Determination of corrosion rate by electrochemical impedance method	MDS_1002	3 days	HN
47	Introduction to petroleum industry for non-professionals	INT_1001	2 days	HN/HCM
48	Writing and presentation skills in scientific research	SSK_1006	3 days	HN/HCM
49	Procurement professionals	SSK_1014	2 days	HN/HCM
50	Training for internal controllers	SSK_2002	5 days	HN/HCM
51	Management skills for middle managers	SSK_1004	7 days	HN
52	Awareness and interpretation of ISO/ISO 14001:2004 and OHSAS 18001:2007	GEN_1007	2 days	HN/HCM
53	Internal audit of ISO/ISO 14001:2004 and OHSAS 18001:2007	GEN_1011	2 days	HN/HCM

Note:

- Customized agenda and topics at your requirement
- Available for in-house training provision
- For any further information, please contact address as below:

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