SOLID-POLYMER-SURFACTANT COMPLEXES FOR ENHANCING THE FLOW IN PIPELINES

ZAINAB YOUSIF SHNAIN

Thesis submitted in fulfilment of the requirements
for the award of the degree of Doctor of Philosophy
(Chemical Engineering)

Faculty of Chemical Engineering and Natural Resources
UNIVERSITI MALAYSIA PAHANG

JULY 2016

ABSTRACT

Eddies which arise as a result of the turbulent nature of fluids pumped through pipelines is a major challenge which contributes to drag. Such not only increases the time of liquid transportation, but contributes to massive energy dissipation. As a result, efforts are being made to contain these anomalies but a consensus has not been reached. Thus, the initiation of this current research. This work introduces an economically feasible technique for enhancing the drag reduction and mechanical degradation of known polymeric additives through the formation of certain complexes with polar surface active agents (surfactants). Such was achieved by using two polymeric additives: Polyacrylamide and Sodium Carboxyl Methyl Cellulose, two surfactants: Sodium Dodecyl-Benzene Sulfonate (SDS) and Triton X-45 and Nano particles of Fumed silica to form complexes. Three phases were involved in the experiment-the use of Rotating Disk Apparatus (RDA) to examine drag reduction, mechanical resistance and stability of the additives, the Transmission Electron Microscopy (TEM) to examine the morphology of the complexes, the drag reduction and shear stability of the investigated solutions using a closed loop pipeline system. Overall, the results obtained from all the stages of the experiment showed that drag reduction increased as the concentration increased. The highest drag reduction for polymer was 48% at 2000ppm while the complex of Polyacrylamide and Sodium dodecyl-benzene sulfonate gave 54% which made complexes better. This showed optimum performance against their 33% and 35% respective individual DR. Adding fume silica to this mixture inhibits their degradation and yielded %DR of (47, 48, 51, 54, 58), (45, 48, 54, 55, 57) and (56, 57, 61, 63, 68) for polymer-surfactant-fumed-silica powder at (500, 1000, 1500, 1700, 2000)PPM concentration respectively.However, the pipe results obtained for 2000ppm was 7826.618. Results for (PAM-Triton X-45-fumed silica) complex was 85.8 % drag reduction and for fumed silica-Triton X-45 complex (fumed silica-PAM), it was 79.2% and 76.7% respectively. Other results such as fumed silica alone, surfactant solution and polymer at 2000ppm showed 63.2 %, 62.6% and 59.5% drag reduction respectively. Overall, about 85.8% DR was achieved in the study, which is the power saving possible in transporting the fluid through pipelines. A mathematical expression was developed to delineate the real mechanism of DR. As a conclusion, new, greener DRAs were successfully introduced and their effectiveness in improving the flow was proven experimentally. According to the TEM images, it is confirmed that complexes are effectively formed in the present work and new aggregated structure can contribute significantly to the drag reduction and polymer shear resistance enhancement.

ABSTRAK

Eddies memberi kesan kepada bendalir dalam saluran paip bergolak adalah cabaran besar dimana menyumbang kepada daya geseran. Bukan sahaja untuk cecair mengalir akan mengambil masa yang lama bahkan tenaga akan mengalami penguraian secara besar-besaran. Berdasarkan keputusan yang diperolehi, usaha yang dibuat mengandungi seperti anomali yang mana kesepakatan tidak dicapai. Maka dengan ini, penyelidikan ini dijalankan. Kajian terkini memperkenalkan teknik yang dilaksanakan dari segi ekonomi untuk mengurangkan daya geseran dan degradasi mekanikal yang dikenali sebagai bahan tambahan polimer melalui pembentukan yang kompleks bersama agen permukaan kutub aktif. Ini dapat dicapai dengan menggunakan dua bahan tambahan polimer, *Polyacrylamide* dan *Sodium Carboxyl Methyl Cellulose*, dua agen permukaan kutub aktif, *Sodium Dodecyl-Benzene Sulfonate (SDS)* dan *Triton X-45* dan zarah nano silica-Fumed untuk membentuk kompleks. Tiga fasa yang terlibat dalam eksperimen ini seperti pergunaan *Rotating Disk Apparatus (RDA)* untuk memeriksa daya geseran dan ketahanan mekanikal dan kestabilan aditif, *Transmission Electron Microspy (TEM)* adalah untuk memeriksa morfologi yang kompleks dan pengurangan daya geseran dan kestabilan rumusan yang dikaji menggunakan sistem saluran paip tertutup. Secara keseluruhannya, keputusan yang diperolehi daripada semua peringkat ujikaji menunjukkan daya geseran dapat dikurangkan apabila kepekatan ditingkatkan. Daya geseran yang paling tinggi diperolehi adalah 48% iaitu 2000 ppm manakala kompleks Polyacrylamide dan Sodium dodecyl-benzene Sulfonate memberi sebanyak 54% menjadikan kompleks yang lebih baik. Ini menunjukkan prestasi yang optimum berbanding 33% dan 35% secara individu DR.*Fume Silica* ditambah ke dalam campuran untuk menghalang degradasi dan penghasilan%Dr 47,48,51,54,58%, (45,48,54,55,57)% dan (56,57,61,63,68) % untuk aditif polimer, serbuk fumed-silica, serbukpolymer-surfactant-fumed silica pada (500,1000,1500,1700,2000) ppm setiap kepekatan. Walau bagaimanapun, keputusan paip diperolehi untuk 2000 ppm pada 7826.618 Re adalah kompeks(*PAM-Triton X-45 Fumed silica*) iaitu 85.8% pengurangan daya geseran dan untuk *Fumed silica-Triton X-45* kompleks, (*Fumed silica-PAM*) adalah 79.2%,76.7% pada Re yang sama. Keputusan yang lain seperti *Fumed Silica*, campuran aditif, polimer pada 2000 ppm menunjukkan 63.2%, 62.6%,59.2% setiap *DR* pada Re yang sama. Secara keseluruhannya, kira-kira 85.8% Dr telah berjaya dicapai dalam kajian ini, yang mana kuasa dapat dijimatkanndalam mengangkut bendalir melalui saluran paip. Ungkapan matematik telah dirumuskan untuk membuktikan mekanisme yang sebenar untuk *DR*. Kesimpulannya, *DRAs* baru telah berjaya diperkenalkan dan keberkesanannyauntukmeningkatpengaliran telahterbultisecara eksperimen.Berdasarkan imej *TEM* telah disahkan bahawa komplek berjaya dibentukkan dalam uji kaji ini dan jumlah struktur yang baru boleh menjadi penyumbang utama kepada pengurangan daya geseran dan peningkatan ketahanan polimer.

TABLE OF CONTENTS

CHAPTER 3 METHODOLOGY

CHAPTER 4 RESULTS AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AMPS	2-Acrylamido-2-methylpropane sulfonic acid
2D	Two dimensional
C	Critical aggregation concentration
CTAB	Acetyltimothyammonium Bromide
CFBRs	Commercial fast breeder reactors
CFD	Computational fluid dynamic
CMC	Carbon methyl cellouse
CTAB	Tetradecyltrimethylammonium bromide
HTAB	hexadecyltrimethylammonium bromide (HTAB)
DHC	District heating or cooling
F	Friction factor
I.D	Internal diameter
Mw	Molecular weight
PAM	Polyacrylamide
SDBS	Sodium dodcyl benzene sulfonate
A	Area, m^2
DR	Drag reduction
RDA	Rotating disk apparatus
Re	Reynolds number
GAE	Glycolic acid ethoxylate lauryl ether.
TEM	Transmission Electron Microscopy
ΔL	Length difference

CHAPTER 1

INTRODUCTION

1.1 Introduction

The most suitable and economic means for transportation of water, crude oil and petroleum products especially over long distances is via pipelines. However, the cost effect of transportation through pipelines is still on the high side mainly because of great power consumptions associated with such modes of transportation. Transporting liquids in strategic pipelines always occur in turbulent mode and that means massive power dissipation during the transportation. One of the oldest techniques for overcoming this problem was through building supporting pumping stations all over the line to regain the dissipated power by re-pumping the liquids. This is considered as a highly power-consuming technique and economically not feasible due to the high additional costs of maintenance and labour.

Over the years, many techniques for reducing drag were suggested by many researchers for a vast majority of applications. One of these methods is based upon suppressing turbulent eddies through the use of baffles with different heights at Turbulent region. In addition, greasy material layers or bubble layers for skin friction reduction have been used in many applications. One of the most effective techniques however, is the addition of small quantities of dilute polymer solutions to liquids that are being transported through pipelines with turbulent flows as this can lead to significant drag-reduction (DR). This was first discovered in (1948) by a renowned researcher, (Tom) and has since enjoyed increased attention. However, detailed explanation of the main mechanism for the action of the polymer and its effect on turbulence is still under criticism due to the chaotic movement of liquids in turbulent flow systems. According to (Zheng and Yan, 2010), there are three techniques through which drag reduction can be carried out; these are the passive, active and interactive. Passive drag reduction techniques were first inspired from nature through simulating the sharkskin structures that were proven experimentally to have an impact in reducing the skin friction. Generally, this technique depends on restructuring the internal surface of the conduits or the external surface of the submerged surfaces that are in direct contact with the flowing liquid. Several models were suggested by scientists to fulfil the flow enhancement requirements like dimples, riblets, oscillating walls and even micro bubbles. The drag reduction performance of most of the passive techniques investigated was not high, with maximum flow enhancement of 15% reported by many scientists in their publications.

Toms et.al (1948) first discovered active drag reduction technique in the 1940s. This technique depends on injecting soluble additives that have viscoelastic properties into the main flow system and many researchers have proven its effectiveness as a drag reduction technique experimentally. Soluble drag reducing agents (DRA) can be classified into two major types which are surfactants and polymers. Polymeric DRA are widely used in commercial pipelines' transportation systems due to its very long chained structure and viscoelasticity. These additives also has their drawbacks where polymeric additives show very low resistance to high shear forces exposed by pumps or even the turbulence structures themselves. The other type of active DRA's are surfactants that have completely different behaviour and structure when compared with polymers. Surfactants or Surface Active Agents are mostly polar short molecules that can form certain type of aggregates called micelles. It is believed that, these micelles have the ability to act, in a way or another, like polymeric DRAs when interacting with the turbulent structures of eddies in the pipe. The resistance of surfactant to high shear forces is very low (lower than the polymers) and their drag reduction performance is lower. However, surfactants have a unique feature that is considered as an advantage when compared with the polymeric DRA, which is its polarity. The surfactant micelles breaks up easily when exposed to high shear forces but can reform themselves after the exposure and that means regaining the drag reduction ability while polymeric additives will lose it permanently due to permanent break in its molecular structure.

Insoluble additives were identified as effective drag reducing agents earlier than the polymer or even surfactants. The successful implementation of the insoluble additives (suspended solids) as drag reducing agent added more complications and criticism to the already established soluble additives flow mechanism. The effectiveness of these suspensions depends on properties such as their density, shape, particle size and concentrations. The early observations of drag reduction used suspensions of natural products such as sediments as well as wood fibre and were motivated by the need to provide accurate hydraulic transport criteria. The attempts to establish the systematic effects of solid concentration, specific gravity and duct dimensions were reported as unsuccessful, quite possibly because the suspended particles were not of uniform and reproducible dimensions and surface texture.

1.2 Problem Statement

The success of using soluble polymeric additives as drag reducing agents encouraged many industries to implement it as an economically feasible and efficient solution to the pumping power losses problem. All that came with its drawbacks also. One of the major drawbacks is the resistance of these additives to the high shear forces exerted by the pumps, valves and even the turbulent structures themselves. The degradation of the polymeric additives is irreversible, and the damage that occurs to the polymer molecule is permanent. The solution for such problem was through adopting two different approaches. The first approach was to re-inject the additives in certain locations along the pipeline to regain the drag reduction effect, and that increased the operation and maintenance costs. The other approach was to modify the polymeric additives themselves using different chemical procedures like grafting. These increased the cost of the additives, but no experimental proofs have been published yet or adopted by the industry. The new approach, the formation of complexes using soluble additives (polymers and surfactants) have adopted by many pharmaceutical and cosmetics industries but have never tested by the transportation (pipeline transportation) industries. Other insoluble additives are attractive solutions for many flow enhancer developers because of the zero effect of these additives on the apparent physical properties of the transported liquids. However, the particles' size, shape, density and degree of buoyancy completely control the choice of the right powder to be used as DRA. Besides that, the major problem with this technique is the high concentration needed in the separation of these solid particles after delivering the product.Therefore, the present work investigates the drag reduction performance and morphology of similarly charged as well as oppositely charged polymer-surfactant complexes. A three-dimensional complex will be formed (using polymers-surfactants and suspended solids) in an attempt to create an enforced complex that can have higher resistance to shear forces. The morphology of the formulated complex is tested using Transmission Electron Microscopy. The drag reduction and mechanical degradation resistance for all the investigated solutions are tested using Rotating Disk Apparatus and closed loop pipeline systems designed and fabricated for the purpose of this work.

1.3 Objectives of Study

The key objectives of this current study are:

1. To evaluate the drag reduction performance of different types of polymers, surfactants, suspended solids and their complexes using rotating disk apparatus and pipeline systems.
2. To evaluate the complexes mechanical stability against high shear forces using rotating disk apparatus and pipe flow systems.
3. To evaluate the morphology of the formulated complexes and the interactive networks formed.
4. To optimize the process parameters through the development of mathematical correlation equation presenting all the experimental data.

1.4 Scope of the Research

There are many important parameters that are targeted to be achieved in this study. The following points clarify the scope of this research..

(i) Elucidate the effect of Polymers (Polyacrylamide and Sodium methyl cellulose), Surfactant (Triton X-45 and Sodium dodecyl benzene sulphate) and solid (Nano fluid) in reducing the drag in turbulent pipe flow individually with concentrations of 500 ,700, 1000 ,1500 and 2000 ppm using rotating disk apparatus and pipe flow system.

(ii) Study the effect of two dimensional complexes (polymer and surfactant) in reducing the drag in turbulent pipe flow. Complexes with concentration of 500, 700, 1000 and 2000 ppm are used to study this effective using rotating disk apparatus and pipe flow system.

(iii) Investigation of the effect of mechanical chain in reducing the drag in turbulent pipe flow with different flow rates.

(iv) Elucidate the effect of three dimensional complexes (polymer - surfactant and Nano solid particles) in reducing the drag in turbulent pipe flow. The complexes with concentration of 500, 700, 1000 ,1500 and 2000 ppm are used to study its effectiveness using rotating disk apparatus and pipe flow system.

(v) Elucidate the morphology of the formulated complexes which use TEM to check the interactive network formed between polymers and surfactants at different concentrations.

(vi) Calculate the friction factor at different Reynolds Numbers.

1.5 Research Contributions

The major significance of this study is to reduce the frictional pressure and solve the energy loss problem in pipelines using a new DR agent. The reduction of the friction drag during flow can greatly decline the cost of pumping energy and cost of pumping station units. The mechanism of DR depends on the addition of substances to the fluid transportation in turbulent flow. This technique has the potential of improving energy consumption in pipe flow system. It will be a huge contribution and of great benefits to the industry by reducing their annual cost and power consumption. The complexes of (Polymer-Surfactant and Nano fluid) are widely used in many industrial applications such as cosmetics, detergents, paints and food, but its applications in drag reduction is not well explored yet. In addition, few authors have written about modified polymer and surfactants, but no study has been reported with Nano solid particle-based polymers and surfactants strengthened with Nano solids such as modified suspended

CHAPTER 1

INTRODUCTION

1.1 Introduction

The most suitable and economic means for transportation of water, crude oil and petroleum products especially over long distances is via pipelines. However, the cost effect of transportation through pipelines is still on the high side mainly because of great power consumptions associated with such modes of transportation. Transporting liquids in strategic pipelines always occur in turbulent mode and that means massive power dissipation during the transportation. One of the oldest techniques for overcoming this problem was through building supporting pumping stations all over the line to regain the dissipated power by re-pumping the liquids. This is considered as a highly power-consuming technique and economically not feasible due to the high additional costs of maintenance and labour.

Over the years, many techniques for reducing drag were suggested by many researchers for a vast majority of applications. One of these methods is based upon suppressing turbulent eddies through the use of baffles with different heights at Turbulent region. In addition, greasy material layers or bubble layers for skin friction reduction have been used in many applications. One of the most effective techniques however, is the addition of small quantities of dilute polymer solutions to liquids that are being transported through pipelines with turbulent flows as this can lead to significant drag-reduction (DR). This was first discovered in (1948) by a renowned researcher, (Tom) and has since enjoyed increased attention. However, detailed explanation of the main mechanism for the action of the polymer and its effect on turbulence is still under criticism due to the chaotic movement of liquids in turbulent flow systems. According to (Zheng and Yan, 2010), there are three techniques through which drag reduction can be carried out; these are the passive, active and interactive. Passive drag reduction techniques were first inspired from nature through simulating the sharkskin structures that were proven experimentally to have an impact in reducing the skin friction. Generally, this technique depends on restructuring the internal surface of the conduits or the external surface of the submerged surfaces that are in direct contact with the flowing liquid. Several models were suggested by scientists to fulfil the flow enhancement requirements like dimples, riblets, oscillating walls and even micro bubbles. The drag reduction performance of most of the passive techniques investigated was not high, with maximum flow enhancement of 15% reported by many scientists in their publications.

Toms et.al (1948) first discovered active drag reduction technique in the 1940s. This technique depends on injecting soluble additives that have viscoelastic properties into the main flow system and many researchers have proven its effectiveness as a drag reduction technique experimentally. Soluble drag reducing agents (DRA) can be classified into two major types which are surfactants and polymers. Polymeric DRA are widely used in commercial pipelines' transportation systems due to its very long chained structure and viscoelasticity. These additives also has their drawbacks where polymeric additives show very low resistance to high shear forces exposed by pumps or even the turbulence structures themselves. The other type of active DRA's are surfactants that have completely different behaviour and structure when compared with polymers. Surfactants or Surface Active Agents are mostly polar short molecules that can form certain type of aggregates called micelles. It is believed that, these micelles have the ability to act, in a way or another, like polymeric DRAs when interacting with the turbulent structures of eddies in the pipe. The resistance of surfactant to high shear forces is very low (lower than the polymers) and their drag reduction performance is lower. However, surfactants have a unique feature that is considered as an advantage when compared with the polymeric DRA, which is its polarity. The surfactant micelles breaks up easily when exposed to high shear forces but can reform themselves after the exposure and that means regaining the drag reduction ability while polymeric additives will lose it permanently due to permanent break in its molecular structure.

Insoluble additives were identified as effective drag reducing agents earlier than the polymer or even surfactants. The successful implementation of the insoluble additives (suspended solids) as drag reducing agent added more complications and criticism to the already established soluble additives flow mechanism. The effectiveness of these suspensions depends on properties such as their density, shape, particle size and concentrations. The early observations of drag reduction used suspensions of natural products such as sediments as well as wood fibre and were motivated by the need to provide accurate hydraulic transport criteria. The attempts to establish the systematic effects of solid concentration, specific gravity and duct dimensions were reported as unsuccessful, quite possibly because the suspended particles were not of uniform and reproducible dimensions and surface texture.

1.2 Problem Statement

The success of using soluble polymeric additives as drag reducing agents encouraged many industries to implement it as an economically feasible and efficient solution to the pumping power losses problem. All that came with its drawbacks also. One of the major drawbacks is the resistance of these additives to the high shear forces exerted by the pumps, valves and even the turbulent structures themselves. The degradation of the polymeric additives is irreversible, and the damage that occurs to the polymer molecule is permanent. The solution for such problem was through adopting two different approaches. The first approach was to re-inject the additives in certain locations along the pipeline to regain the drag reduction effect, and that increased the operation and maintenance costs. The other approach was to modify the polymeric additives themselves using different chemical procedures like grafting. These increased the cost of the additives, but no experimental proofs have been published yet or adopted by the industry. The new approach, the formation of complexes using soluble additives (polymers and surfactants) have adopted by many pharmaceutical and cosmetics industries but have never tested by the transportation (pipeline transportation) industries. Other insoluble additives are attractive solutions for many flow enhancer

CHAPTER 3

METHODOLOGY

3.1 Introduction

This section clarifies the procedures and methods adopted in this study. All the characterization of analytical devices has been discussed which were used in comparative Rheology properties of polymers-surfactant-and Nano solid particle complexes. In the present work, the additive type, powder type, solution flow rate, and the additive concentration and its variables are investigated. Here, the variables of the research work are one type of solvent, one pipe diameter, five additive concentrations, and six different solution flow rates.So this chapter explains all experimental procedures undertaken as well as materials investigated in this current study. Apart from this, the step-by-step approach towards the realization of this, variables investigated, materials used, materials preparation, equipment and is reported in this chapter. In all, there are over 300 sets of experimental runs undertaken for each additive type with respect to flow rates and concentrations. However, only those samples which meet up with the needed standard were taken for further investigation in the pipe. Each run deals with one type of powder, one size of powder, one pipe diameter, one additive concentrations, and six solution flow rates as shown in appendix A. Polymer, surfactant, powder, and complexes were the four additives investigated and added to the tap water with five concentrations, which are 500, 700,1000,1500 and 2000 ppm respectively to water tank. A nano fumed -silica powder (Nano-SiO_2), USA product, with an average size of 0.007µm was also investigated in the present work. Here, the tap water was used as flowing fluid which can be shown in appendix C. The first set of each table was studied without using these additives i.e. pure solvent. The rheological behaviour was examined by Transmission Electronic Microscopy TEM. Visualization technique was carried out at UITM.

3.2 Major Frame Work of The Study

In the present study, the key apparatuses, including the experimental work and the outcomes were explained via well technique based on this diagram. The results of this frame strategy are clarified in the recommendations and conclusions for next studies.

3.3 Materials

All the materials, comprising of polymers, surfactants and Nano silica powder used in this experimental research were supplied by Sigma Aldrich, Malaysia. Although few of the materials were further purified while the remaining categories were used as supplied. Since most of these materials were purchased in solid form, they were further worked on in order to prepare the desired concentrations, and this was done with their gentle dissolution in double deionized water as reported in section 3.5 below. In this work, two types of Polymers, Surfactants and one type of solid Nano particle are chosen to be introduced as drag reduction agent DRA agents. Tap water was used to prepare samples for Polymer-Surfactant- Nano solid particle complex. Five different combinations of Polymers , Surfactant and Fumed –Silica were used to study polymer-surfactant interaction.

3.3.1 Polymers

Two polymers samples were tested in this present study. These are Polyacryl amide (PAM) and Carboxyl methyl cellulose (CMC) solutions were used as non ionic polymer which were purchased from Sigma- Aldrich company, and used without further purification. Two different types of polymers investigated as DR agents in the present work.

(i) Polyacryl amides (PAM)

Polyacrylamide belong to a versatile family of synthetic polymers high infinitely, dissolvable in water and used more worldwide. It is a liquid form with molecular formula (-$CH_2CHCONH_2$-) and derived acryl amide subunits. They could be synthesized as simple crossed-linked or linear-chain structure with the use of N.N' methylenebis acryl amide. Their molecular formula is $(C_3H_5NO)_n$. They form soft gel when hydrated as a result of their high water-absorbent nature. They are as well applied as thickeners or as suspending agents. They have been widely explored by many researchers as drag reduction agents. However, in most of these dilute aqueous solution, they are prone to thermal, chemical and mechanical break up. The physical properties of Polyacrylamide was tabulated in Appendix A.

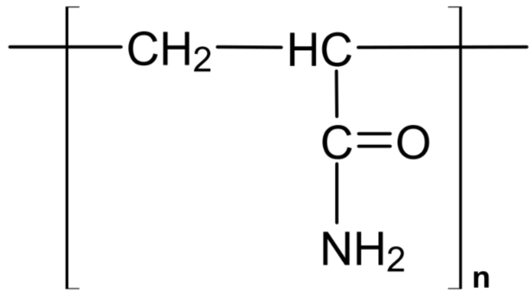

Figure 3.1. Structural formula of Polyacrylamide.

(ii) Sodium Carboxyl methyl cellulose

Sodium Carboxyl methyl cellulose is an anionic polymer. Three grades of Sodium Carboxyl methyl cellulose CMC are available; high viscosity, medium viscosity, and low viscosity. Sodium Carboxyl methyl cellulose CMC is hydrophilic polymer. It is soluble in water but insoluble in organic solvents . Purified sodium carboxyl methyl cellulose is a white or milk colour, tasteless, with a free flowing powder. It is prepared by the method of the reaction of $ClCH_2$ COONa with cellulose hydroxyls. The viscosity of Sodium Carboxyl methyl cellulose CMC solutions increases and decreases reversibly with raising and lowering of temperature, but no permanent change occurs unless the solutions are kept at high temperature for a considerable length of time. Sodium