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JUDUL: **DEVELOPMENT OF BENEFICIATION TECHNIQUE FOR BENTONITE FOR APPLICATIONS IN PETROLEUM INDUSTRY**

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DEVELOPMENT OF BENEFICIATION TECHNIQUE FOR BENTONITE FOR APPLICATIONS IN PETROLEUM INDUSTRY

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Dedicated to my beloved wife Larasati,
my children Lintang, Bimo and Mulia Rahman,
and to my parents and younger sisters

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ABSTRACT

Bentonite from Andrassy and Mansuli area of Sabah had been proven containing higher impurity minerals than commercial bentonite used in petroleum industry. This study comprises an optimum beneficiation process to upgrade the quality of Sabah bentonite by removal of iron and quartz content from it. Several organic acids have been studied but only the oxalic acid can successfully be used. Oxalic acid can be produced by fermentation with filamentous fungi such as *Aspergillus* and *Penicillium*, using as substrate residues with high organic carbon content. The exhaust fermentation medium can be the extracting agent for dissolving the bentonite iron-oxides. This process is economically favourable; besides producing effluents which are easy to purify. Other parameters that included in this study are oxalic acid concentration, beneficiation time, temperature and pH. In general, the optimum conditions for Andrassy and Mansuli samples beneficiation process occurred at an oxalic acid concentration of 7.1 Kg m^{-3} with 2 hours beneficiation time, temperature at 80°C, and a pH less than 2. The results obtained after beneficiation indicated that the content of the montmorillonite mineral from Andrassy and Mansuli sample show improvement with increment from 47 % to 258 % of the original value. The maximum associated silica and iron oxide released with gravitational process are in the range of 2.51% to 11.92% and 1.38% to 13.33%, respectively. The Liquid limit, plastic limit and plasticity index improved varying from 89.82% to 229.63%, 0.40% to 37.13% and 181.78% to 582.57%, respectively. The moisture content and moisture absorption increased in the range of 9.92% to 63.33% and 3.42% to 79.26%, respectively. The cation exchange capacity improved in the range of 22.45 % to 58.54 % and the specific surface area increment from 17% to 104.50%. However, the upgraded sample failed to fulfil the API (American Petroleum Institute) requirements for rheological properties when used as a material in drilling mud and an additive for oilwell cement. Thereafter, certain polymer dispersant had been added to improve rheological properties of the upgraded Sabah bentonite slurry so that it can be used as a drilling mud material and as oilwell cement additive. The YP/PV ratio of the beneficiated samples with addition of 1% to 4% wt Tannathin successfully met the API 13A and 10A requirement. The fluid loss of the beneficiated sample reduced when 2% to 2.5% wt of Tannathin was added. Generally, the degree of improvement of bentonite quality mainly depend on the origin of bentonite itself, it's composition, chemical used in the beneficiation process and it's concentration, beneficiation time, temperature and pH of the solution.

ABSTRAK

Bentonit dari kawasan Andrassy dan Mansuli di Sabah telah dibuktikan mengandungi lebih banyak mineral asing berbanding bentonit komersial yang digunakan dalam industri petroleum. Kajian ini merangkumi proses penceriaan optimum untuk meningkatkan kualiti bentonit Sabah dengan cara mengasingkan besi dan kuarza daripadanya. Beberapa asid organik telah dikaji tetapi didapati hanya asid oksalik yang berjaya digunakan. Asid oksalik boleh dihasilkan daripada fermentasi cendawan seperti *Aspergillus* dan *Penicillium,* digunakan sebagai residu substrat dengan kandungan karbon organik yang tinggi. Medium fermentasi ekzos boleh digunakan sebagai agen penyari untuk melarutkan oksida-oksida besi dalam bentonit. Proses yang berlaku adalah lebih ekonomik, disamping menghasilkan efluen yang mudah dimurnikan. Parameter-parameter lain yang dikaji merangkumi kepekatan asid oksalik, masa penceriaan, suhu dan pH. Umumnya, keadaan optimum bagi proses penceriaan bagi sampel Andrassy dan Mansuli berlaku pada kepekatan asid oksalik 7.1 Kg m^{-3}, masa penceriaan 2 jam pada suhu 80°C dan pH larutan kurang daripada 2. Keputusan yang diperolehi selepas penceriaan menunjukkan peningkatan kandungan mineral montmorillonit antara 47 % sehingga 258 % daripada kandungan asal. Kuarza bersekutu dan besi oksida bersekutu maksimum yang dapat dipindahkan melalui proses gravitasi, masing-masing dalam julat 2.51% hingga 11.92% dan 1.38% hingga 13.33%. Had cecair, had plastik dan indek keplastikan masing-masing meningkat antara 89.82% hingga 229.63%, 0.40% hingga 37.13% dan 181.78% hingga 582.57%. Kandungan lembapan dan jerapan lembapan meningkat masing-masing dalam julat antara 9.92% hingga 63.33% dan 3.42% hingga 79.26%. Kapasiti pertukaran kation pula meningkat dalam julat antara 22.45% hingga 58.54% dan luas permukaan spesifik meningkat antara 17% hingga 104.50%. Bagaimanapun, sampel yang telah dipertingkatkan ini masih gagal memenuhi spesifikasi sifat-sifat reologi yang telah ditetapkan oleh API (American Petroleum Institute) untuk digunakan sebagai bahan bendalir penggerudian dan bahan tambah simen telaga. Oleh yang demikian, polimer penyerak tertentu telah ditambah untuk meningkatkan sifat-sifat reologi buburan bentonit Sabah yang telah ditingkatkan supaya ia boleh digunakan sebagai bahan bendalir penggerudian dan bahan tambah simen telaga. Nisbah YP/PV dari sampel yang telah dipertingkatkan dengan penambahan Tannathin sebanyak 1% hingga 4% berat, berjaya memenuhi spesifikasi API 13A dan 10A. Kehilangan turasan daripada sampel yang telah dipertingkatkan berkurang bila 2% hingga 2.5% berat Tannathin dicampurkan. Amnya, darjah peningkatan kualiti bentonit terutamanya bergantung kepada asal-usul bentonit dan komposisinya, bahan kimia yang digunakan dalam proses penceriaan dan kepekatannya, masa penceriaan, suhu serta pH larutan.

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LIST OF SYMBOLS

A	Interfacial surface area of particle (m^2)
AAS	Atomic Absorption Spectrophotometry
A_{mb}	Area covered by 1 methylene blue molecule (130 Å)
A_v	Avogadro number (6.02 x 10^{23}/mol)
A, b	Constant
C	Concentration (mol l^{-1})
C	Weight of cup (g)
c	Cohesive energy density (kg/m^3)
D	Diffusivity in liquid (cm^{-2} s^{-1})
D	Weight of dish (g)
D_e	Effective diffusivity in solid
D_t	Average diameter of flask (mm)
d	Particle diameter (Å)
E	Activation energy (kg m^2/sec^2)
EDS	Energy Dispersive Spectroscopy (2 θ)
EDX	Energy Dispersive X-ray (2 θ)
ΔH	Heat of vaporization (KJ/hour)
H	Enthalpy (KJ)
IL	Ignition Loss (%)
G	Standard Gibbs energy (KJ/mole)
K	Equilibrium constant
K	Factor obtaining liquid limit from water content
k	Overall mass transfer coefficient
k	*R*eaction rate constant (mol m^{-3} min^{-1})

k_L	Convective mass transfer coefficient
k_1	Forward reaction rate constant
k_2	Backward reaction rate constant
k^{-1}	Thickness of double layer
L	Organic ligand
LL	Liquid Limit (%)
M	Flow rate of total solution mixture (ml/s^2)
MA	Moisture adsorption (%)
MC	Moisture content (%)
N	Mass of inert solid in underflow/mass of solution retained by inert solid
N	Number of Blows
n	Order of reaction
n_o	Bulk concentration
n^+	Concentration of cation
n^-	Concentration of anion
PI	Plasticity Index (%)
PL	Plastic Limit (%)
PV	Plastic Viscosity (cp)
R	Ideal gas constant (0.082 atm.L/mol.K)
R	Radius of particle (Å)
Re	Reynold number (8,314 J/mol.K)
$-r_A$	Chemical reaction rate
SEM	Scanning Electron Microscope
S_s	Specific surface area (m^2/g)
ΔS	Entropy (J/K)
Sc	Schmidt number
SG_b	Specific Gravity of bentonite
Sh	Sherwwod number
T	Heat transfer (J)
T	Temperature (°C or K)

t	time (s)
V_c	Volume filtrate collected between 7.5 and 30 minutes (ml)
Vb	Volume bentonite, (ml)
VF	Volume fraction
V_m	Volume of methylene blue solution (ml)
Vpycno	Volume pycnometer (ml)
V’t	Remaining toluene volume, (ml)
Wo	Weight of picnometer (g)
Wa	Weight of toluene + Wo (g)
Wb	Weight of picnometer + bentonite (g)
Wc	Weight of picnometer + toluene + bentonite (g)
W_N	Water content
W_1	Weight of dish and bentonite sample in room condition (g)
W_2	Weight of wet bentonite sample with cup (g)
W_3	Weight of dish and bentonite sample (dried 105°C) (g)
W_4	Weight of crucible and bentonite sample (dried 105°C) (g)
W_5	Weight of crucible and bentonite sample (fired at 1000°C) (g)
XRD	X-Ray Diffraction (count per second / cps)
YP	Yield Point (lb/100 ft^2)
μ	Viscosity of liquid (cp)
ρ	Density of liquid (g/cm^3)
ρ_b	Density of bentonite (g/cm^3)
$\rho_{toluene}$	Density of toluene (g/cm^3)
υ	Specific resistance per unit mass of precipitated metal
ψ	Electrical potential (ψ>0)

Superscripts

II	Bivalent lattice on the particle surface
III	Trivalent lattice on the particle surface
n+, n-	Valence of aqueous species

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Bentonite is a member of general clay mineral groups and consists of smectite clay and impurities such as gravel, shale, limestone, quartz and other minor minerals (Konta,1995). Bentonite deposits are distributed only in Tertiary formations, especially in The Green Tuff Regions of Miocene age (Sudo and Shimoda, 1978), which formed by devitrification and the accompanying chemical alteration of a glassy igneous material, usually a tuff or volcanic ash and it often contains various proportions of accessory crystal grains that were originally phenocrysts in the volcanic glass (Konta, 1995). These are feldspar (commonly orthoclase and oligoclase), biotite, quartz, pyroxene, zircon and various typical of volcanic rocks. Bentonite crystals have flat thin sheet morphology. The shape of bentonite can be up to 1,000 nm in the largest dimension. However, a side view of the crystal reveals a uniform size of 0.92 nm thicknesses. The result of this morphology is an extremely large surface area of about 800 m^2/g (Luckham and Rossi, 1999). It has found application in various industries, such as drilling mud material, cement additives, ceramic material, foundry molding and etc. The type of bentonite that has been important in an oil and gas industry is sodium bentonite, because of its plasticity. The effect of the bentonite is to slow the progress of water through the soil or rocks. When bentonite mixed with water, it will swell till 40 Å. This property holds a role in a drilling mud, such as;

lifting cuttings and preventing hole problem. The drilling mud must have sufficient density and gel strength to maintain such weighting material in suspension.

With the bentonite, the cement system can successfully placed between the casing and formation, rapid compressive strength development, and adequate zonal isolation during the lifetime of the well. The important considerations in the use of bentonite are the properties that good bentonite gives a lightweight cementing system, minimum free water, good fluid loss control, good rheological properties and adequate compressive strength.

In order to reduce the overall cost of bentonite used in the local oil and gas industry, the feasibility study of local bentonite application had been initiated, especially for the area of Andrassy and Mansuli, Sabah Malaysia. Prior to their usage of Andrassy and Mansuli bentonite, physical and chemical properties and their performance as compared with the commercial bentonite must be determined. If their performance is not as good of commercial bentonite, treatment method should be applied to clean the bentonite mineral from impurities.

The treatment process has a great effect on the swelling capacity of the bentonite mineral and by far the best performance is obtained with sodium-based bentonite mineral, which has sodium as counter ions. If the bentonite mineral contains counter ions other than sodium, the swelling properties, viscosity build-up and filter cake permeability will be adversely affected.

From laboratory investigations, it shown that Andrassy and Mansuli samples have less content of montmorillonite mineral and more impurities material such as quartz, kaolinite, illite, muscovite and hematite and low value of Cation Exchange Capacity (CEC), while the commercial bentonite has more montmorillonite mineral and less impurities materials. In addition the Andrassy and Mansuli samples have low degree of swelling, therefore further study is needed to improved the quality of Andrassy and Mansuli samples (Ariffin Samsuri, *et al*, 2001).

In this study, preliminary test of raw Andrassy and Mansuli samples such as mineralogy composition, physical and chemical properties, chemical composition and performance test as drilling mud material and oilwell cement additive had been determined. It is also necessary to understand the nature of environment and the transportation process of impurities in the bentonite by mean of an extraction test. Design and development of mineralogy, physical and chemical laboratories testing are essential to assess the potential application before suggestion can be made. Subsequently, test was run for the beneficiated Andrassy and Mansuli samples in such application as drilling fluids, and cement slurry. The performance of beneficiated Andrassy and Mansuli samples were compared with performance of the commercial (Wyoming) bentonite as a commercial sample.

1.2 Study Area

The studied areas are located in Tawau and Lahad Datu district of Sabah, Malaysia. Two groups of local bentonite samples were collected, namely Andrassy (SA5) which is located at the longitude of N $4^0$18.97' and latitude E $117^0$57.37' in Tawau district and Mansuli (M4) which is situated at the longitude N$5^0$7.35'and latitude E118^0 12.03' in Lahad Datu district. The sample was collected exactly at 0.5 m depths for SA5 (Andrassy) and M4 (Mansuli) at 0.3 m depths. The field sampling from Mansuli area were taken mainly in area underlain by the Ayer Formation, which collectively form the Segama Group and is interpreted to be Miocene in age (Khairuddin & Radzuan, 1992). The Ayer Formation has two distinction lithofacies; the bedded tuffaceous facies comprising bedded tuff, tuffite, tuffaceous sediment, and volcanic breccias and the polymict boulder-bed facies comprising slump brecia. An additional lithofacies is the calcareous facies comparising the Tempadong Limestone Member, which is occurred as massive lenses within the bedded tuffaceous facies

(Godwin and Yan, 1994). The Andrassy area is underlain mainly by the high level of alluvium and volcanic rock, and occurs in a bed underlying by Pleistocene to Holocene in age (Yusairi & Yan, 1995).

1.3 Problem Statement

In the local oil and gas industry, bentonite is used as a drilling mud material and in an oilwell cement additive. In Malaysia, bentonite is mainly imported from abroad, such as Wyoming from United States, and some other sodium based bentonite from India, Indonesia and Thailand. In order to reduce the dependency of the imported bentonite, the development and production of the local bentonite are sought to be initiated due to long way of transportation and storage.

In addition, the quality assurance of the imported bentonite has been a major problem which cause some problems to the local drilling contractors. Sometimes, the imported bentonite failed to provide the required viscosity and fluid loss control to the drilling mud system and this may cause drilling operation to be interrupted. So, with the production of local bentonite, the quality can be easily maintained and the supply of bentonite also can be assured. In this study, the beneficiation by leaching and gravitational processing had been selected to upgrade the Andrassy and Mansuli samples due to less time need for the process.

Based on forecasting of 50 development and 10 exploration wells will be drilled per year, the requirement for bentonite as an additive is about 16000 tones metric yearly, with the cost of more than RM 15 million per year (Sarimah *et al.*, 2000). With no doubt the production of local bentonite will generate an alternate income, which can increase the gross domestic product (GDP) of Malaysia.

1.4 Objective

The objective of this study is to characterize the raw bentonite, develop beneficiation technique and evaluate its efficiency and evaluate economic significant of the technique in order to produce good quality of the Andrassy and Mansuli bentonite so that it can be beneficiated as a drilling mud material and additive in oilwell cement industry.

1.5 Scope of Study

1. Five sources of samples had been used in this study, four samples namely SA5-1, SA5-3, SA5-4 and SA5-7 from Andrassy of Tawau area and the other sample namely M4 from Mansuli of Lahad Datu Sabah.

2. Prior to the beneficiation process, the pre-beneficiation of iron and quartz were performed. This is important because the iron and quartz contents of Mansuli and Andrassy samples are higher than the commercial bentonite.

3. After pre-beneficiation, beneficiation process was developed to remove impurities so that Andrassy and Mansuli samples have less impurity and then activated with polymer extender variety in order to improve the bentonite viscosity.

4. After beneficiation process, the beneficiated samples were subjected to a series of testing based on American Petroleum Institute (API) RP 13A specification as drilling mud material and API 10A for an oilwell cement additive.

5. Comparisons were carried out between the performance of beneficiated Andrassy and Mansuli samples, and commercial bentonite.

6. Economic analysis were carried out to look at promising economic potential of the Sabah bentonite.

1.6 Thesis Organization

This thesis consists of six chapters, and the contents of each chapter is explained as follows:

CHAPTER 1: This introductory chapter presents the significance of this study, study area, problem statement, objective and scope of study.

CHAPTER 2: Presents theoretical study of beneficiation process and description of the mineralogy, physical and chemical test, including general test procedures of Specific Surface Area (SSA), XRD, and Atomic Absorption Spectroscopy (AAS) studies.

CHAPTER 3: This chapter reviews details of the bentonite mineral performance and API testing as a drilling mud material and an oilwell cement additive

CHAPTER 4: This chapter describes the beneficiation process methodology and the test procedures. The effect of each extractant solvent will be discussed and assessed in detail. The result gained will view the potential of Andrassy and Mansuli bentonite usage in petroleum industry.

CHAPTER 5: This chapter will evaluate the effect of organic acid parameter to the samples. The properties of raw samples will give an overview of early assessment. The designed procedures will suggest the optimum beneficiation process for application in drilling mud operation and cement additive technology.

CHAPTER 6: This chapter summarizes the main conclusions of the study and the recommendations for future research.