X-Ray Fluorescence (XRF) to identify chemical analysis of minerals in Buton island, SE Sulawesi, Indonesia

Jamaluddin¹, A Darwis², M A Massinai³

¹Geological Engineering Department, School of Geosciences, China University of Petroleum, Qingdao, China.
²Physics of Department, Science and Technology Faculty, Alauddin Islamic State University of Makassar, Makassar, Indonesia.
³Geophysics Department, Science and Mathematic Faculty, Hasanuddin University, Makassar, Indonesia.
E-mail: jamaljumaluddin1994@gmail.com

Abstract. Asbuton as natural rock asphalt consists of a granular material; usually limestone or sandstone. In its natural state, it contains bitumen intimately dispersed throughout its mass, while the remainder of the material is a solid mineral matter. This research was conducted in Sorowallo, Buton Regency, Southeast Sulawesi province, Indonesia. This study aims to determine the content and the percentage of minerals contained in the rocks by using X-Ray Fluorescence (XRF). The method of research is a preliminary survey, sampling and laboratory analysis. XRF reports chemical composition, including Si (quartz) and Ca (calcite). The results indicate the content and the percentage of element dominate the rock sample is Fe₂O₃, MgO, CaO, and SiO₂. Research results using XRF show that there are four metal oxide dominant elements. Hematite (Fe₂O₃) is dominant in all locations of sampling. Magnesium oxide (MgO) has the highest levels found in sample number six and the lowest is in sample number five. Silicates (SiO) has the highest levels at sample number six and the lowest in sample number seven. Calcium oxide (CaO) is dominant in all sampling locations. The sample of asbuton contains 37.90% asphalt, 43.28% carbonate, and 18.82% other minerals.

1. Introduction

Buton asphalt deposits exist in large quantities in Buton Island, South-East Sulawesi, Indonesia, and it is named locally as “asphalt buton” or “asbuton”. Since the deposits are widely vary in both composition and properties, the production of a consistently uniform material [1]. The main geological units that outcrop in the study area include Winto Formation and Sampolakosa Formation. Buton has been interpreted to record one or more collisions of microcontinents with the Sundaland margin in the Cenozoic. Deformed metamorphic, ophiolitic and Mesozoic sedimentary rocks are overlain by deep water Neogene sediments, and there are asphalt deposits and oil and gas seeps which are probably generated from Triassic source rocks.

Indonesia is one of the countries that has the largest reserve of natural asphalt in the world. Asphalt reserve in Indonesia may reach up to 677 million tons, then it is able to support road infrastructure in this country up to 200 years to come [2]. Moreover, the constructions of road infrastructure is expected to continue in the future. The addition of Buton Granular Asphalt (BGA) in the mix has a significant effect in decreasing the fatigue performance in terms of initial maximum strain compare to the fatigue performance of mixes using pure petroleum bitumen or pure refinery asbuton bitumen [3]. This shows that asbuton is a great potential for this country. However, it has not been able to be fully used up to
now. The deposit of solid bitumen resources are approximately 60,991,554.38 tons (24,352,833.07 barrel oil equivalent). The solid bitumen resources are deposited in the lime-sandstone of the Tondo Formation and in the sandy-limestone rock of Sampolakosa Formation. The both formation sources are likely to come from Winto Formation (Triassic) and are considered as the solid bitumen-bearing formation [4].

The Buton-Tukang Besi region of Sulawesi has long been recognised to be a micro continental block of Australia. New regional models suggest that there was a collision in the Late Oligocene-Early Miocene but that Neogene deformation was primarily extensional, which could account for the observed deformation in a different way from earlier interpretations. Instead of slicing off several microcontinents from New Guinea and multiple collisions, it is suggested that there was a single early collision followed by crustal extension of an upper plate probably driven by subduction rollback in the Banda Arc. Offshore multibeam and seismic data support the extensional models but field work on Buton and Muna is required to test earlier and new suggestions by re-examining stratigraphic and structural relationships, constructing accurate cross-sections, and determining timing and character of tectonic events.

Figure 1. Geological map of Buton Island [5].

2. Method
The method of research is a field survey, sampling, and laboratory to using X-Ray Fluorescence (XRF) analysis. A field survey is the systematic investigation of the geology beneath a given piece of ground for the purpose of creating a geological map or model. The data used in this research is the primary data. The location of the sampling done directly at some points in Buton Island based on field survey and determination of location before using Google earth and the Global Positioning System (GPS). It is done to find the location of the distribution of the samples that have been taken.

The spectroscopic method can also be combined with X-ray fluorescence (XRF) or geochemistry data to determine the chemical compositions of rocks. XRF can also sometimes be used to determine the thickness and composition of layers and coatings. The method is fast, accurate, not destructive, and
usually requires only a minimum of sample preparation. Applications are very broad and include the materials science and food industries along with ore mining, geochemistry, and environmental analysis of water and waste materials. XRF spectrometer systems can be divided into two main groups: Energy dispersive system (EDXRF) and wavelength dispersive system (WDXRF). The total measurement time for a single XRF analysis depends on the number of elements to be determined and the required accuracy and varies between 2000 to 5000 s. XRF is a very sensitive technique and but samples must be free of contamination [6].

3. Result and discussions
This research has been conducted in laboratory test on each rock samples using X-Ray Fluorescence (XRF) which will be analyzed the content of metal oxides as well as referring to the State of the regional geology research. The result can be seen in the table below, that basically consists of approximately 30% of bitumen and 70% of minerals such as limestone or sandstone.

| Sample | Compound metal oxide (m/m%) |
|--------|-----------------------------|
|        | Fe$_2$O$_3$ | MgO | SiO$_2$ | CaO |
| 1      | 39.07       | 27.18 | 22.80 | 5.78 |
| 2      | 39.96       | 25.74 | 25.50 | 3.47 |
| 3      | 5.56        | 0    | 0     | 89.46 |
| 4      | 44.39       | 0    | 0     | 5.46 |
| 5      | 12.79       | 12.79 | 0     | 76.78 |
| 6      | 36.37       | 28.03 | 29.37 | 0.644 |
| 7      | 6.99        | 0    | 4.01  | 71.86 |

A refining process without the addition of the petroleum asphalt can reduce the mineral content to produce another form of Buton asphalt. The results of XRF analysis show that seven samples have the same element content in Table 1. The concentration of oxides in different buton rock asphalts is presented in Table 1. Asphalt content in asbuton rock is 37.86%. The average content of carbonate solids found in asbuton rocks is 43.28%. Therefore, asbuton rock contains 37.86% asphalt, 43.28% carbonate solids, and 18.86% other impurities. Other impurities could have been solid SiO$_2$, CaSO$_4$, CaS, and others. These solids have very low solubility in water and acid when compared with carbonate solids. This cause other impurities still remain in the asphalt. In the previous study, asbuton rock from Lawele were previously found to contain mineral and asphalt. Asphalt from asbuton rock has high viscosity because the asphaltene content is high. On the average, asbuton rock contain 30.08% asphalt and 9.92% mineral [7].

The CaO content decreases with the increase of other oxides present in the limestones. This calcium may be due to the leaching of calcium by solution and subsequent reprecipitation. Change of environment is indicated by the increase of SiO$_2$ content with the influx of terrigenous material [8]. The presence of Fe$_2$O$_3$ and high Ca indicates reducing environment and deposition in closed basin. The presence of little amount of phosphate and manganese in the limestone indicates a warm and humid climate during the deposition of carbonate sediments [9]. Fe$_2$O$_3$ correlates positively with S and authigenic minerals (pyrite, marcasite, calcite, gypsum). The abundance of Fe in coal is related mainly to the occurrence of Fe-bearing minerals such as: (1) authigenic Fe sulphides; (2) authigenic Fe carbonates; (3) Fe sulphates and oxyhydroxides resulted from weathering of Fe sulphides and carbonates; or (4) detrital Fe-containing montmorillonite, chloride, oxyhydroxides, and spinel. Some organic Fe occurrence in coal has also been inferred. The positive correlation of Fe with Fe-bearing
minerals is obvious, whereas the correlation of Fe with calcite and gypsum is probably connected with the common mineral assemblage in coal, namely Fe sulfides – calcite and their weathering products. These rocks derived from alkaline igneous rocks and many contain elements of Fe or iron mixed and react with elements that can lead to the occurrence of oxidation process and electrolysis as by Cl and O on the conditions of the tropical-subtropical climates.

The results of the samples analysis in some places revealed average value of CaO of 36.20% with average levels of MgO 23.43%. The use of chemical agents to react with the minerals was found to be much more expensive and difficult to control the product, since certain chemical agents reacted to a particular mineral only, while usually, about 15 – 20% of the minerals were not limestone. Besides, some acid compounds chosen was also reactive to the metal equipment used in the process [10].

Figure 2. (a) FE-SEM results for asbuton and (b) asphalt product. [10].

Figure 2 shows the FE-SEM result for asbuton and asphalt products. This image is similar to the morphology of a mixture of heavy oil, sand, and other aggregates in Canada. Asbuton extraction with acidic brine water reduced the number of carbonate solids. This is supported by the comparison between Figure 4 (a) and 4 (b). In Figure 4 (a), the morphology of asbuton surface is very uneven or irregular because many mineral solids are stuck to the asphalt. The presence of asphalt can be shown in the dark-colored crevice between the solids. Solids stuck to asphalt have sizes at the micro scale. Figure 4 (b) shows that the morphology of asphalt surface is flatter than asbuton surface. This image is also like liquid surface similar to the physical characteristics of asphalt. In the surface asphalt can be seen clearly and little solids stick to the asphalt, unlike asbuton surface [11].

The presence of limestone (with a high Ca content) in the rock asphalt indicates an increased of pores size that suggest the rock has resistive properties. The presence of Ca innate element, in the asphalt rock, may have contributed to the bonding or adhesive of asphalt and the composition of this chemical element is used for the production of cement materials.

4. Conclusions
Asphalt buton rock contains 30.08% asphalt and 9.92% mineral. The mineral in asbuton rock are CaO$_2$, MgO$_2$, H$_2$O, SiO$_2$, and Fe$_2$O$_3$. Asbuton is natural asphalt from Buton island with great deposits and can be utilized, as a road material because it contains not only bitumen but also mineral with high lime content (CaCO$_3$). The mineral asbuton will cause an environmental problem if it is not utilized properly.
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