ARTICLE IN PRESS

Egyptian Journal of Petroleum (2016) xxx, xxx–xxx

HOSTED BY

ELSEVIER

Egyptian Petroleum Research Institute

Egyptian Journal of Petroleum

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www.sciencedirect.com

FULL LENGTH ARTICLE

Characterization of bitumen samples from four deposits in southwest, Nigeria using trace metals

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Received 26 May 2016; revised 1 August 2016; accepted 18 August 2016

KEYWORDS

Bitumen;
Oxic;
Terrestrial;
Atomic absorption spectroscopy;
Trace metals

Abstract Bitumen samples collected from different locations in south-western Nigeria were analysed for trace metal constituents such as Fe, Pb, Cu, Cd, Ni, Mn and V using Atomic absorption spectroscopy. The concentration of Fe ranged from 38.00 to 1537.00 ppm, Pb ranged from 11.00 to 27.00 ppm, Cu ranged from 3.00 to 10.00 ppm, Cd ranged from 4.00 to 15.00 ppm, Ni ranged from 9.00 to 62.00 ppm, Mn varied between 3.00 and 6.00 ppm, V ranged 10.00–150.00 ppm. Some ratios of these trace metals such as V/Ni, V/(V + Ni) and Fe/V were calculated, and the results show V/Ni ranged from 0.24 to 16.67, V/(V + Ni) varied from 0.20 to 0.94 and Fe/V ranged from 3.8 to 15.37. The low values of V/Ni ratios of samples AB, OI and IL suggest high maturity, mixed marine and terrestrial source of bitumen while the calculated values of V/(V + Ni) suggest that the samples were formed under oxic condition. The results were correlated using Pearson's correlation matrix. A high positive correlation among the four bitumen samples indicates that they are geologically and genetically related.

1. Introduction

Bitumen is a mixture of organic liquids that are highly viscous, black, sticky and partly soluble in carbon disulphide. Although no two bitumen are chemically identical and chemical analysis cannot be used to define the exact chemical composition of bitumen, elemental analysis indicates that most bitumens contain 79–88% carbon; 7–13% hydrogen, traces to 3% nitrogen; 8% sulphur; 8% oxygen by weight, it is substantially soluble in some solvents such as carbon disulphide and trichloroethylene and become molten when heated [1]. Natural bitumen forms from oil which are already generated and migrated into reservoirs and are subjected to other effects as well as normal maturation processes, these additional changes occur when the continuity of the reservoir horizons permit either up deep or down deep gas to come in contact with the oil accumulation, one of such processes is known as water washing, which occurs when the reservoir trap is in contact with moving meteoric water. The process is simply the flushing away of the lighter hydrocarbon compounds in an amount proportional to their solubility. The result is a big decrease in gasoline range hydrocarbon content and decrease in light asphaltenes and aromatics. This, in turn, produces an environment of a dense

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Peer review under responsibility of Egyptian Petroleum Research Institute.

http://dx.doi.org/10.1016/j.ejpe.2016.08.002
1110-0621

component and a reduction of API gravity so that heavy oil devoid of light component is the result (bitumen).

Trace element data of crude oils have been reported to be effective in classifying and correlating oil and are relative to organic geochemical methods [2–9]. The nature of occurrence of metals, their distribution patterns and concentrations in crude oils and petroleum oils can give information on the origin, migration, the environment of deposition and maturation of petroleum [5,7,10]. Trace metals are incorporated into oils in the form of porphyrin complexes (species) in petroleum source rocks and may include direct incorporation from the biomass and formation during sedimentation [8]. It may also involve diagenesis from organic molecules as well as metals derived from biogenic (biomass) and abiogenic (weathering of minerals) sources. Lewan [3], has shown that source rock, type of organic matter and depositional environment have profound effects on the concentration of trace elements in source rocks. There may be difficulty in correlating oils and or/source rocks using trace elements contents. However, metals of proven association with organic matter may be used as reliable correlation tools. Nickel, Vanadium, and Cobalt (usually referred to as biophile elements) are such examples. The concentration of metals in bitumen oil can be used to classify oils into families.

The purpose of this study is to determine the trace metal constituents of bitumen samples from south western Nigeria and apply them to ascertain the maturity trend, the source and genetic relationship.

2. Materials and methods

2.1. Description of study area

Bitumen samples were collected from four different locations, Ilubirin, Agbabu, Loda, and Ode-Irele sites, where bitumen outcrops occur. These samples were collected in November 2015 with glass vials with Teflon caps and preserved in a refrigerator at a temperature of less 4 °C prior to laboratory analysis. The study area falls between longitudes 4048′ and 4054′ E and between latitudes 6035′ and 6039′ N (Fig. 1). It is an area of lowlands with few ridges, about the lowlands; the hills are very high which are characteristic of the tropical rainforest of southwestern Nigeria. The temperature is relatively high during the dry season with the temperature reaching about 30 °C. The harmattan brought in the northeasterly winds from December to February, which has ameliorating effects on the dry season high temperatures. The area is well drained by NE–SW trending rivers such as Omilala, Ogun, Shasha, Oba, and Opeki. The area falls within the 1:50,000 standard topographic sheets 282 (Okitipupa south-east). Each sample location was plotted using a global positioning system.

2.2. Sample collection and analyses

The four bitumen samples selected for the study were collected from the richest bitumen spots from four villages all in Odigbo Local Government Area of Ondo State, Nigeria. One sample was collected from a standard extraction hole drilled by early explorers of bitumen in Agbabu village (AB), the second sample was collected from a drilled well in Ode-Irele (OI), the third sample was collected from clear outcrop deposits in a waterlogged area on the outskirt of Ilubirin (IL) and finally one sample was collected from clear outcrop deposits in a waterlogged area on the outskirt of Loda (LD) (Fig. 1). Trace metal determination in bitumen samples was carried out by using dry ashing, dilution in organic solvents method [22,23]. Five grams (5 g) of the bitumen samples were weighed in porcelain crucibles that were preheated on a hot plate at a temperature of 130 °C for 4–5 h. 2 mls sulphuric acid was added and then waited to perform the charring at 180 °C. The samples were then ashed in a muffle furnace at 650 °C for about 6 h. The ash was dissolved in 5 ml of HCl, and the material was transferred into calibrated flasks and diluted to the 50 ml mark with deionized water [24]. The product was a colourless liquid and was taken to the laboratory for trace metal analysis using Varian Atomic Absorption Spectrophotometer (Spectra AA-200).

3. Results and discussion

The concentration of trace metals in bitumen samples are shown in Table 1, while Pearson's correlation matrix of trace metals in bitumen samples and API gravity is given in Table 2. Trace metals have been employed in crude oil characterization and oil-oil correlation studies [4–7,11]. Copper ranges from 3.00 to10.00 mg/kg. These values are lower than the values obtained by Obiajunwa and Nwachukwu [12]. Iron concentrations range from 38.00 to 1537.00 mg/kg. The values are higher than those of Ipinmoroti and Aiyesanmi [13] and Adebiyi and Omole [14]. Nickel concentrations range from 9.00 to 62.00 mg/kg. The value of vanadium ranges from 10.00 to 150.00 mg/kg. The relatively high levels of Ni, Fe, and V observed in the result should be expected because these metals are commonly associated with petroleum with an abundant input of porphyrin – precursor chlorophylls to the organic matter [15].

Furthermore, most soils around bitumen deposits in Nigeria are also associated with substantial deposits of metal ores such as iron. A relatively high level of Ni and V > (100 mg/kg) has been reported to be associated with most petroleum oil samples obtained from the marine environment [5]. Bitumen samples from Ilubirin and Loda study sites were obtained from waterlogged areas. It is also possible that intense rainfall and flooding which are regular occurrences of the area under study could have contributed to the leaching of most trace metals and contributed to the enhanced level of these metals. This, therefore, justifies the relatively high levels of Ni and V in the bitumen samples compared to other metals investigated.

The concentrations of most of the metals as contained in Table 1 differ from those obtained by Obiajunwa and Nwachukwu [12], Ipinmoroti and Aiyesanmi [13] and Adebiyi and Omole [14]. The difference may be due to the fact that earlier studies of these researchers mentioned, were made of the bituminous sand while the present study used bitumen obtained from apparent outcrops. The process of extraction of bitumen from bituminous sand might leach out some metals from the bitumen, hence, the relatively lower concentrations of some metals reported by these researchers.

Please cite this article in press as: M.C. Onojake et al., Characterization of bitumen samples from four deposits in southwest, Nigeria using trace metals, Egypt. J. Petrol. (2016), http://dx.doi.org/10.1016/j.ejpe.2016.08.002