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AN EVALUATION OF THE HOT AQUEOUS CAUSTIC LEACHING OF NIGERIAN ONDO TAR SAND

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Abstract

Nigeria is endowed with a large deposit of tar sand in Ondo state, the response to leaching beneficiation treatment has not been elaborated. In this work, samples of tar sand from Ondo state was leached with sodium hydroxide and sodium carbonate as a preliminary step and thereafter with sodium hydroxide at varying contact times and molar concentrations. The bitumen samples as-received and as-leached were also subjected to solubility tests using toluene. The results obtained showed that sodium hydroxide gave a higher percentage bitumen recovery of 48% as against 20.95% for sodium carbonate for the same leach contact time. The highest percentage recovery of bitumen of 53.50% and minimum percent bitumen loss of 1.95 was obtained at mass ratio of 1: 10 of sodium hydroxide to tar sand and 15 minutes contact time. The solubility test showed that the leached bitumen was 97.70% pure and this implies a removal of about 92.43% of mineral matter in the bitumen. The high purity of the bitumen concentrate obtained is significant as the tar sand was sourced from a shallow pit and the leaching was carried out at the less expensive normal atmospheric pressure. The results obtained thus indicate that a much higher concentration ratio may be attained for deeper and less contaminated deposits subjected to high pressure autoclave leaching.

Keywords: tar sand; leaching; contact time; concentrations; solubility; bitumen.

1. Introduction

Tar sand, also known as bituminous sand, is a type of unconventional petroleum deposits. It is a naturally occurring mixture of sand, clay, water and a dense and viscous form of petroleum technically referred to as bitumen. Tar sand has also been described as oil impregnated sandstone. Physically, tar sand consists of sand grains surrounded by a bituminous film. Tar sand is found in large amounts worldwide but in exceptionally large quantities in Canada and Venezuela. Nigeria is also reported to have the second largest deposit of tar sand in the world containing about 41 billion barrels of oil found in cretaceous ferruginous sediments extending over about 120 km from Ogun state, across Ondo state to the margin of Edo state [1, 2, 3].

Bitumen can be extracted from tar sand by the hot water extraction process, in which the displacement of the bitumen is achieved by wetting the surface of the grain with an aqueous solution containing a caustic wetting agent such as hydroxide, carbonate or silicate of sodium. The resulting strong surface hydration forces developed on the sand particles cause the displacement of the bitumen in the aqueous phase. The second stage phase separation of the bitumen was accomplished by a modified froth flotation technique. The by-products derivable on processing tar sand include asphalt, synthetic crude oil, sulphur, phenol and pitch [4].

Bitumen is used primarily for paving roads and for the production of water proofing products, such as roofing felts and for sealing flat roofs. As a result of the increase in oil price since 2003, upgrading of bitumen to synthetic crude has become economical. Considering the scarcity of prime coking coals, bitumen extract has also been used as additive to upgrade medium coking coals to cokeable grade for cokemaking. The Nigerian market for bitumen has been estimated at about 150,000 per annum [3, 5]. The amount of bitumen contained in tar sand can be determined by solubility test. Trichloroethylene was once commonly used for the solubility test, but concerns over the toxicity of halogenated hydro-carbons necessitated its substitution with aromatic hydrocarbons such as toluene and xylene. Owolabi [6] used carbon tetrachloride for the solubility test.

The magnetic stirrer apparatus has one or more fixed electromagnets that generate a rotating magnetic field enclosed in housing. The electromagnets generate a rotating magnetic field which in turn transmits the rotational movement to the stirring member situated in the stirring vessel and thus initiate and maintains the stirring operation [7]. The Stuart Scientific SM3 magnetic stirrer hot plate consists of a cast aluminium hot plate with a maximum temperature of 400°C. The unit has a built-in magnetic stirrer with variable speed up to 1,300 rpm. The SM3 model of Stuart magnetic stirrer hot plate has speed and hot plate control knobs [2]. In view of the large deposit of tar sand in Ondo state and the potential applications of bitumen extracts, this research is aimed at developing a caustic leaching route for the efficient and economic recovery of the bitumen entrained in it.

2. Materials and methods

2.1 Materials

The basic material used in this work was lumps of tar sand obtained from Ondo state Nigeria.

2.1.1 Sample collection

About 13 kg lumps of semi-solid black tar sand were collected from an open pit (after the overburden sand was removed) at a depth of 20 cm in Gbeleju Loda village in Irele Local Government area of Ondo state. Irele Local Government is on the eastern boundary of Okitipupa Local Government which lies on longitude 40º 3" East of Greenwhich Meridian and Latitude 50º 45" and 80 º 15" North of the Equator. After the field sampling, the lumps of tar sand obtained was kept in large plastic bags.

2.1.2 Sample preparation

The tar sand lumps were thoroughly homogenized and then left to dry in air prior to removal of experimental samples.

2.2 Methods

The leaching tests (by gravimetric approach) carried out on the homogenized tar sand are described below.

2.2.1 Effects of molar concentrations on bitumen leaching rate

2 g of the homogenized air dried tar sand was reacted in aqueous solution obtained from a 1:20 mass ratio of sodium carbonate to tar sand (that is derivative 0.038M sodium carbonate). The mixture of the tar sand, water and sodium carbonate was then homogenized by stirring for about 5 minutes and then leached on magnetic stirrer hot plate (without a magnetic bar) for 15 minutes. The typical heating profile(at the combination of temperature and stirrer speed used) for the solvent distilled water on the magnetic stirrer hot plate is shown in Fig. 1. The bitumen that was separated during heating floated to the surface of the leaching solution and was removed by careful sedimentation of the tailings and decan-tation of the bitumen onto Dr Watt filter paper. The residual bitumen on the tailings was thereafter dissolved with toluene. The bitumen and tailings recovered were air dried overnight and then dried by slow heating on the hot plate. The test described was again carried out with sodium hydroxide. The results obtained are presented in Fig. 2.

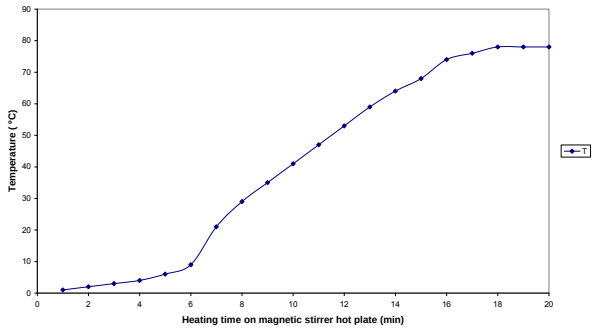

Fig. 1:Heating profile of distilled water on the magnetic stirrer hot plate

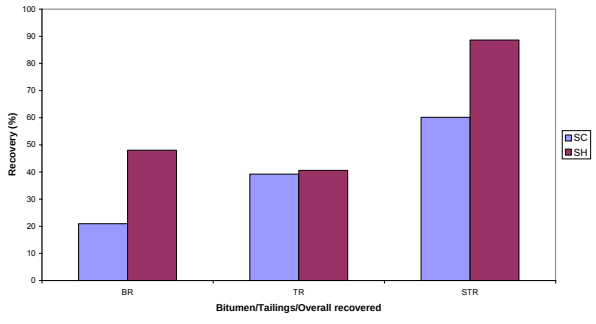

Fig. 2: Relative leaching potency of sodium carbonate (SC) and sodium hydroxide (SH) on Ondo tar sand

In addition, the procedure described above was repeated using 1 g of tar sand in a 25 ml aqueous solution with reagent to tar sand mass ratio of 1: 10 (that is, derivative0.1M sodium hydroxide) for 5 minutes. The test procedure was also repeated four more times

but using derivative 0.06, 0.08, 0.12 and 0.14M sodium hydroxide, respectively for 15 minutes in each case. The results obtained on the effects of sodium hydroxides molar concentrations on bitumen recovery % are presented in Fig. 3.

2.2.2 Leaching contact time

The initial procedure described above was repeated using 1 g of tar sand in an aqueous solution with reagent to tar sand mass ratio of 1: 10 (that is, derivative 0.1M sodium hydroxide) for 5 minutes. The procedure was again repeated four more times for contact times of 10, 15, 30 and 45 minutes. The results obtained on the effects of leaching contact time on bitumen recovery % are presented in Fig. 4.

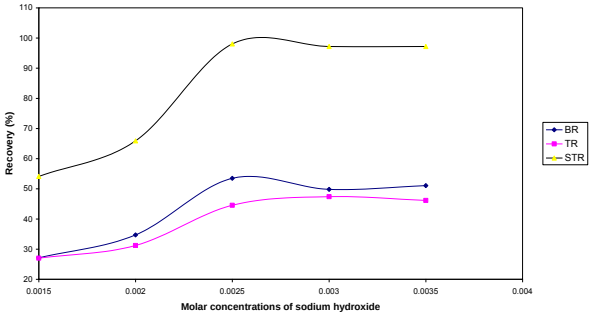

Fig. 3: Effect of molar concentrations on the bitumen (BR), tailings (TR) and total recoveries (TR) (%) in sodium hydroxide leaching of Ondo tar sand

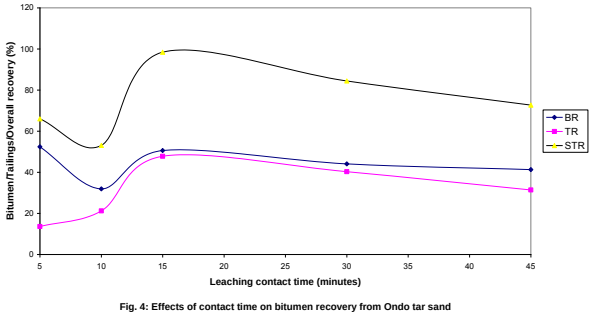

Fig. 4: Effects of contact time on bitumen recovery from Ondo tar sand

LEGEND:
BR = Bitumen recovery curve, TR = Tailings recovery curve, STR = Overall recovery curve

2.2.3 Bitumen solubility test

The solubility test was conducted using the modified form of ASTM D2042. 1 g of air dried bitumen extract was placed in a 250 ml beaker and 5 ml of toluene was added to it. The mixture was left for about 15 minutes to allow for the dissolution of bitumen in the tar sand. The solution obtained was filtered with a Dr. Watt's filter paper. The residue of mineral tailings obtained was then dried and weighed. The procedure described was further repeated four more times but for 10, 15, 20 and 25 ml of toluene. The as-received tar sand sample was similarly treated. The results obtained for bitumen solubility at varying volumes of toluene are presented in Fig. 5, while percents of gangue and bitumen recovered for as-received and leached bitumen are shown in Figure 6.

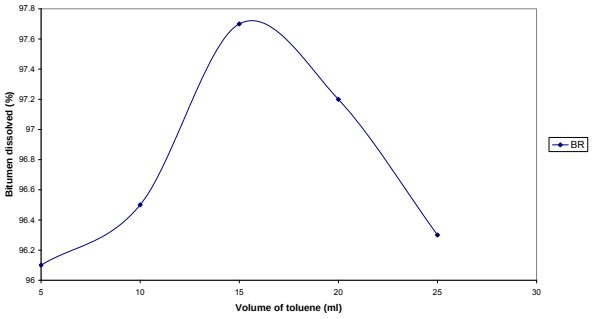

Fig. 5: Effects of volumetric concentrations of toluene on bitumen solubility (BR) in Ondo tar sand

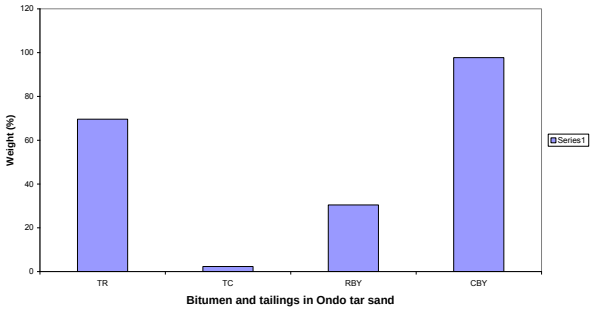

Fig. 6: Yields of tailings (in raw tar sand TR, leached TC) and bitumen (in raw tar sand RBY and leached CBY)

3. Results and Discussion

The results obtained are presented figures 1 to 6. The leaching of Ondo bitumen with sodium carbonate gave percentage bitumen, tailings and total recoveries of 20.95, 39.20, 60.15 respectively, while sodium hydroxide yielded 48.00, 40.60 and 88.60; respectively, at 1:10 mass ratio of reagent to tar sand (Fig. 2). The results obtained showed that sodium hydroxide produced the higher recovery of bitumen with the lower percentage of bitumen lost on washing with toluene. On the basis of the results obtained, sodium hydroxide can be said to produce stronger surface hydration forces on the sand particles than sodium carbonate to cause the displacement of the bitumen in the aqueous phase with Ondo tar sand. Abramov *et al* [8] and Sepulveda *et al* [3] used sodium hydroxide, sodium carbonate and sodium silicate to extract bitumen from tar sand and crude oil.

The results obtained on the dependence of bitumen displacement from tar sand on molar concentrations of sodium hydroxide (Fig. 3) showed that percentage bitumen recovery increased from 27.10 at derivative 0.6M sodium hydroxide to the maximum of 53.55 at derivative 0.1M and then decreased to the lowest of 49.80 at derivative 0.12M.

The results obtained thus indicated an initial increase in bitumen recovery followed by a slight decrease. The initial increase in bitumen recovery followed by a decrease showed that the interfacial hydration forces created by sodium hydroxide attained an optimum strength at a particular concentration. Abramov *et al* [8] indicated that the optimal recovery of bitumen and crude oil from tar sand and contaminated sandy soil occurs at a particular molar concentration of sodium silicate.

The results obtained for bitumen recovery dependence on leaching contact time (Fig. 4) showed that percentage bitumen, tailings and total recovery increase from 40.40%, 22.70%, 63.10% at 10 minutes contact time to the maximum of 53.50%, 44.55%, and 98.05%; respectively at 15 minutes contact time. The bitumen losses percentages of 36.90, 1.95, 15.70 and 25.00 were obtained at 10, 15, 30 and 45 minutes respectively. The results obtained thus showed that the leaching contact time of 15 minutes not only produced the highest bitumen recovery but also gave the least bitumen loss. For the aqueous leaching of Indian Assam coal, leaching rate of ash and sulphur has been reported to generally increase with increasing contact time [9].

The deviation observed in the behaviour of bitumen on leaching from tar sand in comparison to coal may be due to the difference in the leaching mechanisms involved in both cases. While the leaching of ash and sulphur from coal occur by dissolution reaction at the coal/reagent interface, the displacement of bitumen from tar sand has been reported to take place by the development of surface hydration forces at the bitumen/sand interface [3]. The decrease in bitumen displacement with increased contact time might have been due to decrease in the interfacial hydration forces developed at increasing contact time.

For the solubility test, the lowest weight of tailings was obtained at 15 ml of toluene with the highest percent bitumen recovery of 97.70%. This implies that the highest recovery of bitumen occurred at this volume of toluene for the weight of tar sand used. The percent bitumen recovery obtained is very close to 99.60 and 99.05 reported by Owolabi [6] for plain liquid Ondo bitumen obtained from wells A and B in Lamudifa village, Odigbo Local Government Area of Ondo state. The solubility test on the as-received and leached bitumen showed that the gangue in the raw bitumen was reduced by about 92.43% with a bitumen purity of 97.70%.

4. Conclusions

The Nigerian Ondo bitumen bearing tar sand has been successfully leached sodium hydroxide to produce a concentrate containing 97.70% organic matter which translates to a mineral matter reduction of about 92.43%. The tests conducted showed that derivative 0.1M sodium hydroxide at 15 minutes contact time produced the highest percentage bitumen recovery. The organic content of the tar sand bitumen is only 1.90% lower than about 99.60% determined for pure liquid Ondo bitumen. It can thus be deduced that Ondo bitumen can be readily stripped from the associated sand in a dilute alkaline solution.

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