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G.S.P.L.A.J

"Knowledge is a natural right
of every human being"

FOREWORD

On behalf of the Petroleum Research Centre, I have great pleasure to introduce the first issue of the Petroleum Research Journal to the scientific community at large. The publication of this Journal is intended to enhance existing knowledge and to promote available means of exchanging scientific information of interest on both national and international levels.

The Petroleum Research Centre is affiliated directly to the National Oil Corporation. Some of the main areas of activities of the centre include research in exploration, exploitation, drilling, processing, petrochemical, corrosion & pollution studies, also, economic evaluation studies related to oil industries, in addition to analysing and testing oil products and petrochemicals according to international specifications and standards.

Finally, I would like to thank the members of the Editorial Board for their successful efforts in getting this issue in the present form. I, also, take this opportunity to invite local and outside researchers to contribute in the development and progress of this Journal, I hope they will find their contributions in future issues of this Journal encouraging and professionally rewarding.

Dr. Mustafa Sola
General Manager

PETROLEUM RESEARCH JOURNAL

Editorial Policies

The Petroleum Research Journal (PRJ) is a multidisplinary scientific technical journal published periodically by the Petroleum Research Centre. The aim of the journal is to publish articles classified as original papers and short notes, of both practical and theoretical interests, which deal with scientific and technical advances in the fields of geology, geophysics, geochemistry, chemistry, petroleum and chemical engineering. Subject matter should be relevant to hydrocarbon exploration, evaluation and industry.

– Ideas of the preliminary results of investigation that have not advanced yet, to the point at which they warrant publication as a f ull paper, may be submitted for puplication as short notes.

– All contributions submitted in Arabic or in English, and which conform to the guidelines given in the instruction to authors are considered.

– Technical contributions are accepted with the understanding that they have not been published elsewhere, and are not currently under consideration by another journal nor will be submitted to another journal while under consideration for PRJ.

– All technical manuscripts and short notes are processed by the Editor – in – Chief. Three copies of each submitted manuscript are sent to the appropriate Associate Editor for technical review. The Associate Editor will seek evaluation from three reviewers qualified to judge the technical value of the paper. He then, collects the reviews received,synthesize their contents, and make a recommendation to the Editor – in – Chief concerning the acceptability of the manuscript. The final decisioin on a paper's disposition is then made by the Editor – in – Chief and communicated to the author (s) within one week.

— Twenty five reprints of each article published will be supplied to each contributor free of charge.

Instruction to Authors

Conformity to the following instructions is a prerequisite for publication :

I. An original and three copies of each technical paper and short note, complete with original and three copies of illustrations, list of references, and list of figure captions are to be submitted to the Editorial Board of the journal.

II. A title page should accompany the text, which includes the title of the paper (the title should be as informative and brief as possible), followed by the author (s) name and place of employment.

III. Regular manuscripts require an abstract (in Arabic and in English) approximately 100–200 words, short notes do not. the abstract should emphasize the conclusion reached in the paper.

IV. Manuscripts are to be typed double–spaced one side only. Ample margin should be left at the top and bottom. Equations except simple ones that a typewriter or word processor can handle, should be printed in hand by black ink.

V. Illustrations including photographs, charts and diagrams are to be submitted in 21x28 cm format. They should accompany the manuscript but should not be inserted in the text.
Illustrations are to be referred as 'Figures', and should be numbered consecutively in the order in which they are referred to in the text. Brief captions should be provided to make the figures as informative as possible.

1. All line drawings should be made with black drawing on white paper (preferably tracing paper). Computer-drawn illustrations are acceptable. The author's last name should be written on the margins (or on back) for identification.

2. Photographs (which must be kept to minimum) should be glossy prints. The author's last name and identification as to which is the top of the picture is to be written in pencil on the back.
A list of figure and table captions are to be typed on a separate page and attached at the end of the manuscript. List the figure number in the form "Fig.I".

VI. In the manuscript, principal headings should be typed at the centre of the page in capital letters. Headings of the text lower rank should be typed in small letters (first word of headings and proper nouns are capitalised). The following text should begin on the next line. For headings of lower rank underline and place a dash after the headings, and follow with text on the same line.

VII. All references should be grouped at the end of the paper, under the heading *References,* either alphabetically or by the numerals noted in the text. For a given author referred more than once, use chronological listing with suffix, a, b,etc., to distinguish references of the same year. In the list of references, the following order and punctuation should be observed :

For paper from journals :

- author(s) name (last name first, then initials),
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Example :

Wilson, H.H., 1975, Time of Hydrocarbon Expulsion: Bull., Assoc. Petr. Geol., v 59, p 69-84.

For reference to books :

- author (s) name (as above),
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Yuen, C.K. and Fraser, D., 1979, Digital Spectral Analysis: Pitman Publishing Limited.

For references to a paper within a book :

- author (s) name,
- year of publication,
- title (of paper/optional, in (followed by)
- editor,
- title (of book) :
- publisher,
- page umber.

Example :

Baker , D. and Carter, V., 1972, seismic velocity anisotropy, in Heard, H. and Raleigh, B., Eds. Flow and Fracture of rocks : Geophys. Mono 16, Union, p 157-166.

VIII. All correspondence should be addressed to :

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Editorial

The idea to introduce a multidisplinary technical Journal devoted to the advancemet of all aspects of research related to hydrocarbon exploration and industry, was set in motion couple of years ago , during several meetings which included the General Manager of the Petroleum Research Centre and the chairmen of the various scientific committees in the Centre . There was basically no benefits , but there was the belief that there would be in time if such aims of high quality publications are achieved .. This is our goal .

As excited as we are about introducing Volume 1, Number 1, issue, we are keenly aware that effective evolution of this publication depends on the responsiveness and active participation of the contributors and the readers alike . We look forward for their contributions, and constructive ideas for improving our issues. The painstaking efforts of our distinguished reviewers is the source of our aspirations .

Editor - in - Chief

PRJ, Vol 1, (January 1989) ; P. 4–10, 10 FIGS.

SUSCEPTIBILITY OF WELDING JOINTS TO STRESS CORROSION CRACKING IN AERATED 3.5% NaCl WATER SOLUTION

A. Mazur * and A. Esayed *

قابلية الوصلات الملحومة للتآكل الشرخى بالاجهاد عند تعرضها لمحلول من الماء وكلوريد الصوديوم بتركيز 3,5٪

د . آدم مازور و أ . السيد

لم يتم بوضوح حتى الآن معرفة قابلية الوصلات الملحومه للفولاذ المنخفض الكربون للتآكل الشرخى بالاجهاد حيث يعتبر هذا النوع من الفولاذ عادة غير قابل للتآكل الشرخى . ولكن عدة انهيارات حدثت فى المناطق الملحومه . ويمكن أن يعزى ذلك نتيجة لنمو شروخ طفيفة تكون سببا لانتشار شرخى مفاجىء . تعرض هذه الدراسة نتائج الجزء الأول من الابحاث التى أنجزت على صفائح فولاذية مقطوعة وملحومه بسمك 40 مم تم تعرضها لمحلول من الماء وكلوريد الصوديوم بتركز 3,5٪ . تم وضع العينات المراد تحليلها فى منطقة الانصهار وعلى شكل رقم سبعة وأختبرت بطريقة الكتيفة المعلقة تحت ظروف الدائرة المفتوحة ، هذا وقد لوحظ أن انتشار الشروخ بالتآكل الشرخى بالاجهاد يتغير بوضوح عندما تنتقل الشروخ من منطقة الانصهار والمنطقة المتأثرة بالحرارة الى منطقة الفولاذ الأصيل . وقد وجد أن نسبة قابلية التآكل الشرخى بالاجهاد تساوى 0.72 حيث تنتمى هذه القيمة الى أعلى تصنيف لقابلية التآكل الشرخى بالاجهاد لهذا الفولاذ . ويعتقد هنا أن آلية انتشار الشروخ كان نتيجة مجتمعة بين قصافة الفولاذ بتأثير الهيدروجين بسبب وجود بنية المارتنسايت والبينايت والمسارات النشطة المتواجدة قديما اينما تواجدت بنية المارتنسايت والبينايت .

ABSTRACT

Susceptibility of welding joints of low-carbon steels to stress-corrosion cracking (SCC) is not clearly established. Such steels are generally not susceptible for that type of corrosion, but many failures have been observed in welding zones where subcritical crack growth was suspected to be a cause of catastrophical crack propagation. This work consists of the first set of research results performed on samples cut from welded 40 mm thick steel sheets exposed to a 3.5% NaCl water solution. The specimens with the tip of a V notch placed in a fusion zone were tested by the cantilever beam method in an open circuit condition. The mechanism of SCC susceptibility ratio K_{SCC} / K_C *was 0.72. This value belongs to the highest class of susceptibility to SCC. The mechanism of crack propagation is believed to be a mixed mode of "hydrogen induced embrittlement" due to bainitic (or martensitic) structures and "pre-existing active path" where the pearlite and ferrite structures are present.*

INTRODUCTION

Stress-corrosion exhibits a very specific mechanism involving a particular environment and tensile stresses applied to the metallic construction. There will be no fracture if only a stress or corrosive environment is present. For a particular environment the stress-corrosion cracking (SCC) will appear if the metallic construction is loaded by sufficiently high tensile stresses. Below some critical stress level, stress-corrosion cracks will not start to grow. Actually, the best measure of the material's sensitivity to stress-corrosion cracking is the ratio K_{ISCC} / K_{IC}. The value of K_{ISCC} represents a maximum of stress of fracture toughness, which can be safely applied to construction in a specific environment without producing a SCC during long periods of time. Usually the standard testing-time is 1000 hours. Although stress-corrosion is not the only type of material degradation but the form of such attacks are always dangerous. A very localized crack is often propagating thoughout

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the cross-section of the construction without alarming marks visible on the metals surface. Such a crack can be initiated on the metallic surface at the tip of a corrosion pit or at any of the sharply ended microdefects.

If applied loads are lower than yield limit but still higher than the critical stress (in terms of K_{ISCC}), the stress-corrosion crack grows slowly until it reaches a critical length and then propagates very fast (catastrophically) throughout the whole cross-section of the construction. Sometimes the period of slow-crack growth is very long. According to (1), a large number of pipe-lines and pressurized installations failed catastrophically only when five or more year of service-time passed. The routine corrosion inspections can hardly discover a stress-corrosion attack, especially if the surface of the steel member is covered by general corrosion products or other types of deposits.

High strength steels consisting of bainite and tempered martensite are generally highly susceptible to stress-corrosion cracking especially if the environment is cathodically promoting evolution of atomic hydrogen at the surface of steel. Therefore, it is believed that hydrogen induced stress-corrosion cracking is the leading mechanism of catastrophical trans-granular fractures of this steel grade. Weldable low-carbon steels are also susceptible to stress-corrosion but in very specific environonments such as highly concentrated caustics (2) and nitrate solutions (3), and anhydrous ammonia (4). The laboratory experiment on welded structures have indicated that the residual stress relief streatments can reduce the susceptibility of such steels to SCC in the above mentioned environments (5). According to the general opinion, weldable low carbon steels are not significantly susceptible to SCC in sea-water or in 3.5% NaCl water solutions. This implies that the rate of the other types of corrosion is higher than the rate of SCC. Such an opinion is based on the results obtained for steel sheets or bars that did not consider the experimental work conducted on welded joints. Internal stresses, segregations and other in homogenities and nonequilibrium structures like martensite and bainite are usually associated with welding joints, strongly promoting SCC in NaCl water solutions with a pH value lower than 7. In modern steel structures welding technology is commonly used. Such welding joints should have similar or better properties than the parent steel to be joined. Of the many failures that have been initiated in the welding areas, some of them had been of a purely mechanical (or metallurgical) origin, but a great many exhibited a typical appearance suggesting that the environment in combination with stresses produced catastrophical crack growth.

Assuming that the engineering calculations and material selection was correct and the safety margin properly applied, the welded construction should be safely used for decades. However, case histories provide many examples of serious failures of welded structures after quite a long period of service-time without characteristic traces of fatigue fracture or general corrosion action. Such long delayed fracture phenomenon should be connected with subcritical crack growth. That crack is nucleating in the areas of weldments characterized by detrimental factors such as mentioned above; chemical and structrual inhomogenities, discontinuities, etc. This is the reason why the results of SCC tests conducted on parent metals are not valid with respect to welding joints. Lack of well elaborated and published data concerning SCC of weldments has been the main reason of the experimental project performed by the Petroleum Research Centre in Tripoli. A part of this project was done with the cooperation of the al Fateh University (6).

MATERIAL

The material tested was a semi-killed steel of a chemical composition typical for SAE 1008 steel grade : 0.10% C max, 0.25 - 0.50% Mn, 0.10% Si max, 0.04% P max, and 0.05% S max. The hot rolled-steel sheet of 40mm thickness had mechanical characteristics as follows : tensile strength Rm = 303.4 MPa, yield strength Re = 168.9 MPa, elongation A5 = 30%, reduction in area Z = 55%, Vickers hardness HV = 170, critical stress-intensity factor (fracture toughness) K_{IC} = 95 − 110 MPam½. Grain-size accroding to ASTM scale was of No.5. The central zone of steel sheet contained a great number of elongated non-metallic inclusions (NMI) and inhomogeneities.

WELDING TECHNOLOGY

The two 40mm thick steel plates of 1000 mm × 1000 mm in size were horizontally welded together, using a manual arc-welding method. The expected heat-affected zone (HAZ) properties did not recommend preheating and postheating treatments. A 60° V- groove was cold machined. For the root-pass, the electrode E - 6018 was selected. For the first and following passes the E- 7018 electrodes have been used. Before welding, the electrodes were dried at an elevated temperature to avoid hydrogen (cold) cracking.

SAMPLING

Figure 1 shows the geometry of specimens cut off the welded steel sheet. They were mechanically grinded applying cooling water and then the mechanical notch of 40° and 5mm in depth was machined. The notch was cut parallel to the welding direction and perpendicularly to the rolling direction of steel sheet. At the notch tip, the narrow 1.5mm in length fissure was cut-in as a place where the stress-corrosion crack

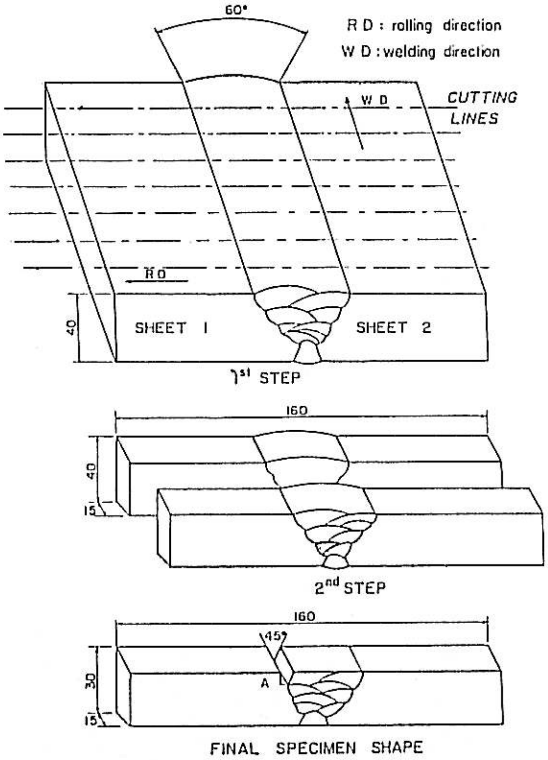

FIG. 1. Sampling and geometry of the specimens.

will nucleate. The welding and sampling processes were made at the Az-Zawiya Refinery.

METHODS

The Cantilever beam method was selected due to its great advantage over the other types of SCC tests that have been used . Such a method provides the following information :

i) Critical stress-intensity factor for SCC (K_{Iscc}),
ii) Stress-corrosion sensitivity ratio (K_{Iscc} / K_{IC}) . If this value is low, the sensitivity of the material to SCC is high .
iii) Time to failure of the steel structure of equal (or smaller) thickness to the tested specimen under known load and environment,
iv) Master-curve of stress-corrosion crack propagation can be derived .

Assuming that SCC are propagating by the brittle or quasi-brittle mode, the Brown's formula (7) for plain-strain conditions will not necessarily be fulfilled . A sketch of the cantilever beam stand is shown in Fig.2. Deflection of the beam was mechanically measured with an accuracy of 0.01 mm. This deflection is proportional to the SCC extension. Initial stress-intensity factor k_{Ii} was calculated according to the formula (8) :

$$K_{Ii} = (4.12\ M\ (\propto^{-3} - \propto^{3})^{1/2}) \ / \ B\ (W)^{3/2}$$

Where :

$M = Pd + (gd^2)/2$
d = lever length, (m)
M = momentum, (MN m)
g = (lever weight (MN)) / (lever length (m))

B = specimen thickness, (m)
W = specimen width, (m)
P = Load applied, (MN)
a = crack length, (m)
$a = K_m + K_f$, (m)
K_m = length of mechanical notch, (m)
K_f = length of precrack, (m)
$\propto$ = geometrical factor

$$\propto = 1 - (a / W)$$

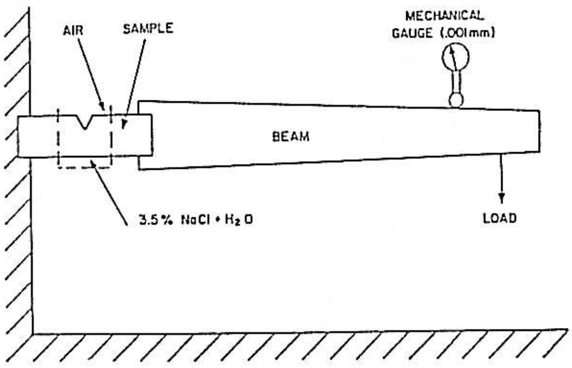

FIG. 2. Scheme of the cantilever beam test.

ENVIRONMENT

An atmosphere containing chloride ions is one of the most corrosive ones. The rate of pittting and general corrosion rate in such an atmosphere (pH below 7) for low-carbon steel is much higher than the rate of SCC. For a fully controlled, standard environment; a 3.5% NaCl water solution is very commonly used, however in some works (9), such a solution should not be considered as a standard one, but none the less a water solution of 3.5% NaCl can represent the atmosphere of marine and coastal areas as well as other environments of ahigh salinity level.

Some works performed on high strength steels gave evidences that the severity of such an environment is increased by its aeration (10). Therefore. in this experiment an aerated water solution of 3.5% NaCl has been used. The measured pH was about 6.5 The stress-corrosion cracking was tested in an open-circuit condition. The solution was exchanged for a fresh one every 24 hours.

RESULTS

A photomacrograph of welding joint cross-section is shown in Fig.3. Well done welding passes are visible there. Shaddowed area enveloping the weld-bead consists of a heat-affected zone. The quality of welding workmanship was very good. Elongated macrodiscontinuities due to chemical segregation and a great amount of NMI are expected in the central area of the base steel sheet which is marked by arrows. The presence of such inclusions was confirmed by microobservation of a cross-section taken from the central area of the tested sheet (Fig.4.) These defects vanished close to the fusion zone (FZ). Obviously, the elongated discontinuities should have a great influence on the corrosion crack propagation in the parent steel sheet. This suggestion leads to special attention payed during analysis of the mechanism of SCC propagation in tested specimens.

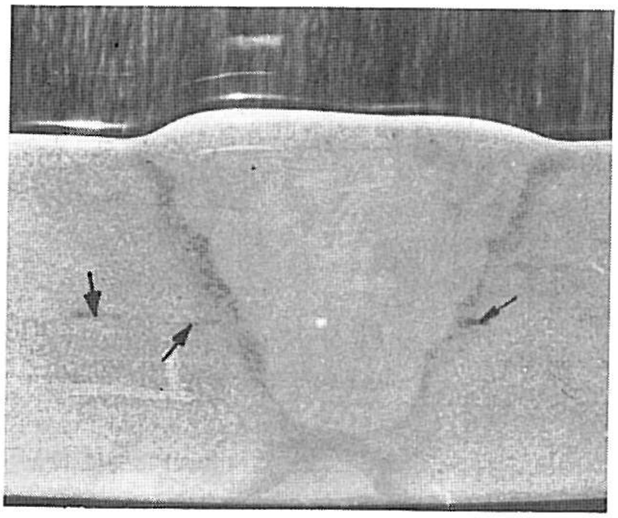

FIG. 3. Macrophotography of welding joint.

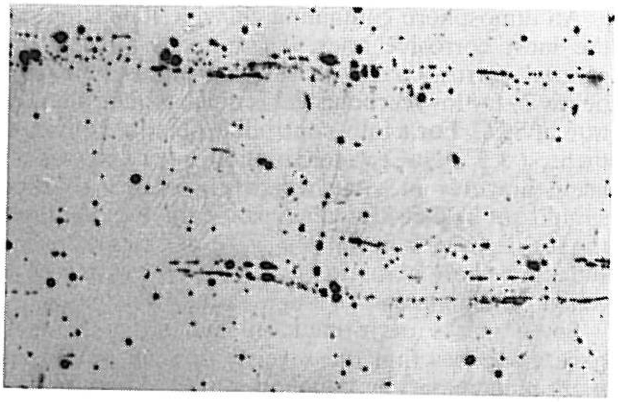

FIG. 4. Non-metallic inclusions in the mid-section of the steel sheet. Non-etched, magnification 100x

Optical microscopic observation revealed different structural constituents present in HAZ and in the parent steel. Figure 5. shows a typical ferrite-pearlite structure in the parent steel. It was possible to find out that the steel sheet was hot-rolled at the temperature well over Ac_3 and then slowly cooled through transition Ac_3 – Ac_1 temperatures that produced the typical widemanstatten structure. HAZ consists of some amount of upper bainite (Fig.6) and ferrite of different shapes and sizes with some pearlitic structure distributed at the ferritic grain-boundaries.

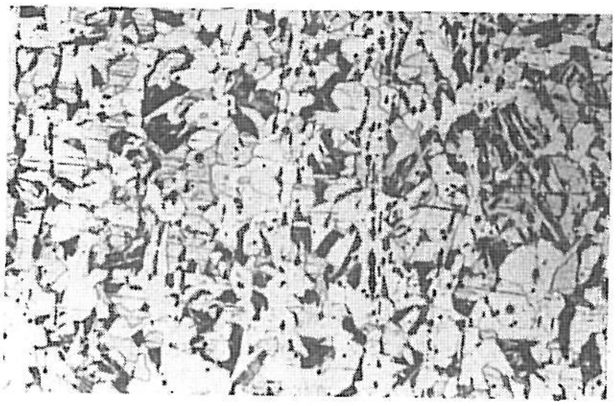

FIG. 5. Ferrite and pearlite structure in the parent steel nital etched, magnification 100x.

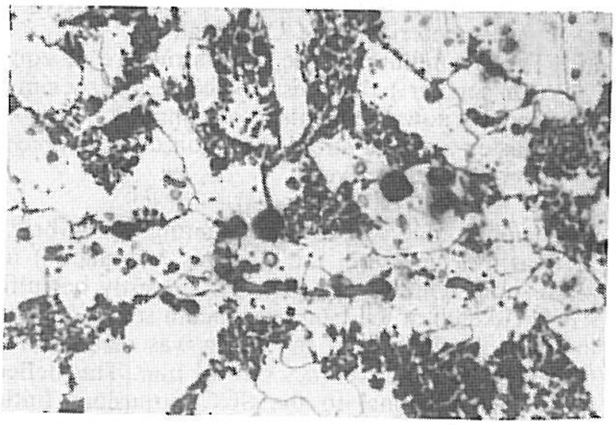

FIG. 6 Ferrite and upper bainite structure with some amount of pearlite in HAZ, nital etched, magnification 250x.

Figure 7 shows a graph of hardness distribution along the three different lines (a,b,c,) passing the weld, HAZ and parent steel. Hardness numbers were higher in HAZ and weld areas than in the parent steel. Some of the higher hardness numbers in parent steel were due to plastic deformation in the notch area produced by mechanical machining as well as by plastic zone developed during the crack propagation. Results of SCC tests are presented in Fig. 8. The resultant K_{SCC} value is 68.4 MPa m ½ with an accuracy of ± 3.16 MPa m ½. The sensitivity of the tested joints to SCC (K_{SCC} / K_{IC}) was 0.723 (± 0.03) According to (10) such values belong to the highest class of susceptibility (0.78 – 0.62). It is important to note that K_{SCC} is the resultant value of SCC phenomenon performed in the three zones : fusion zone, HAZ and parent steel sheet. Assuming that low-carbon weldable steels (parent sheet) are not very sensitive to SCC in a 3.5% water solution of NaCl, the decrement of K_{IC} should be due to the stress-corrosion crack propagation in the fusion and heat-affected zones. Existence of such zones with bainitic and martensitic structures decreases the K_{SCC} / K_{IC} ratio proportionally to the fraction of the crack length passing those zones in comparison with the whole path of the SCC. The exact measure of the SCC crack path-length in particular zones gave results as follows : FZ – 4.8mm, HAZ – 2.4mm, parent steel – 5.2mm. Thus, the fraction of stress-corrosion crack propagated in the most sensitive zones (FZ and HAZ) is 0.58. The upper limit of the stress-corrosion sensitivity ratio is 0.95 (The lowest sensitivity of parent steel to SCC). If the whole SCC hypothetically propagated in FZ and HAZ, that expected sensitivity ratio would be 0.56. That is a very high sensitivity of such areas to SCC and any welded structure should be calculated taking into account this value. Microscopic observation revealed that the typical hydrogen induced mixture of trans and intergranular crack-path in FZ and HAZ, changed to a completely intergranular mode in the parent sheet steel where "preexisting active path"

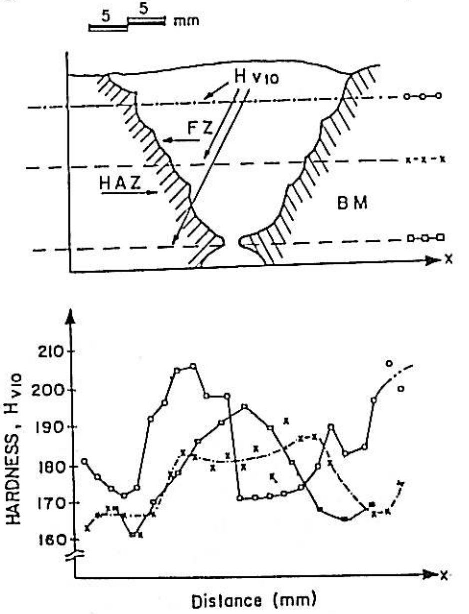

FIG. 7 Distribution of hardness numbers measured along the three lines across the weldbead, HAZ and fusion zone.

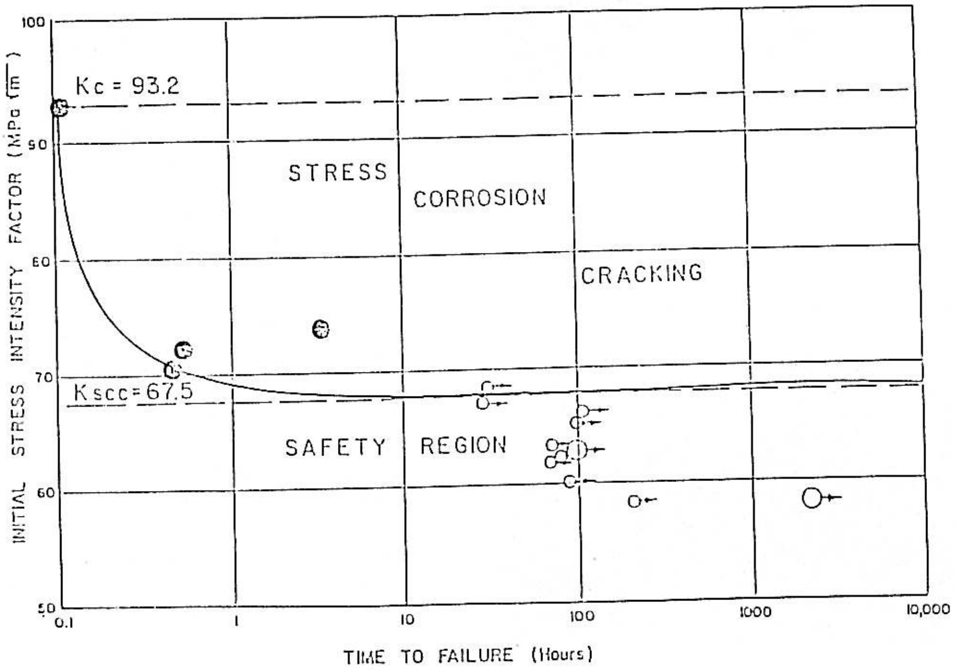

FIG. 8. Results of SCC measurement in form of graph : K_I against time to failure.

mechanism prevailed. As it was mentioned before, the NMI are playing a significant role in SCC propagation. Main crack terminates when meeting a sizable inclusion that sometimes deviates its direction or produces microbranches. Fig. 9 shows a micrograph of an unetched cross-section. The crack started at the point A according to the stress concentration concept (or K_{IC} concept) and stopped at point B where the crack met a segregation area, and started to develop a branch C by electrochemical model of dissolution. That process decreases the rate of crack propagation due to the blunting effects at the crack tip. As the stress concentration at the tip of the branch C decreased, the tensile stress component at point B increased, therefore the mechanical factor prevailed and the higher crack propagation rate in the branch D is observed. In branch D there was a lack of blunting processes. Fig. 10 shows the reaction between a main stress-corrosion crack and the NMI. The non-metallic inclusions usually are cathodic sites and surrounding areas are anodic ones. Therefore the dissolution process is advanced there. This process is strongly time-dependent involving transport phenomenon which needs contact with the environment through very clear visible tunnels.

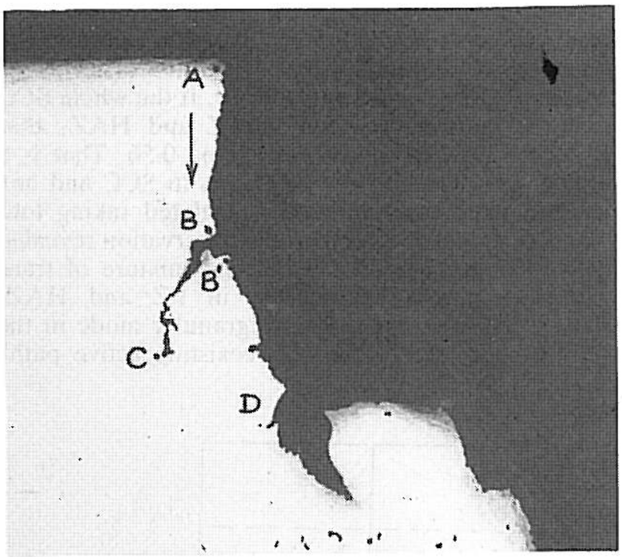

FIG. 9. Stress-corrosion crack passing the segregation area, non-etched, magnification 50x.

FIG. 10. Dissolution process advanced in segregation area. The tunnels are joining a main crack and non-metallic inclusions delivering electrolite to the microcells : NMI are cathodic, ferrite matrix is anodic. Nital etched, magnification 250x.

DISCUSSION

Many investigations were carried out on SCC of ferrite-pearlite low-strength steels exposed mostly to the environments of high pH values. A number of SCC tests made in NaCl solutions with a pH below 7 or in a marine atmosphere were limited to unnotched specimens. A general conclusion of these last results is that low-strength steels are not sensitive to SCC. It means that corrosion failures happened by the other types of corrosion as for instance pitting, crevice or general corrosion.

If the constructions (structures) made of low-strength weldable steels are considered as consisting of hundreds of welding joints, it is necessary to test such special areas (joints) for their susceptibility to SCC. The reason is that welding joints consist often of different structural constituents in the bead and HAZ (bainite, martensite) which have decidedly higher sensitivity to SCC than parent sheet steel with ferrite-pearlite structures. On top of that, welding joints are characterized by different types of segregation, differences in the grain-sizes, NMI distribution and a high level of internal stress. All these factors tend to accelerate stress-corrosion crack growth. The number of specimens tested by the cantilever beam method in the case of very inhomogeneous samples (weldment case) should be as much as possible. Such a method is a long-term one and for the first part of this project the number of experiments was very restricted just to realize that welding joints are very sensitive to SCC. Steel sheet chosen for welding has been produced from semi-killed grade steel and unfortunately the microstructure includes a large number of NMI concentrated mostly in the mid-section area. The majority of the NMI had an elongated shape due to the directionality of the hot-rolling process.

The trajectory of crack propagating from the mechanical notch was perpendicular to the above mentioned NMI direction Therefore if a stress-corrosion crack met a NMI, the local stress situation abruptly changed due to a) blunting effect which decreases stress concentration there (crack will be arrested), b) simultaneously the electrochemical reactions between NMI (cathode) and surrounded iron matrix (anode) will change the crack fissure, creating an elongated hole. That will additionally decrease the stress concentration at the crack tip. Both effects were observed. Sometimes at the arrested crack, the slow process of "branching“ formation was noticed. The next step of crack propagation usually started from the tip of the one branch formed in some area, where due to the segregations, the electrochemical reactions produced a sharp pit. Such a pitend (tip) becomes a stress-riser enabling the crack to propagate again. The front of the crack passing throughout the cross-section does not have a straight line shape but depends upon local properties in the micro-areas of the structure and it changed due to the microstructural and chemical segregations, NMI volume fraction, their shape and distribution. Such structural and chemical segregations are very characteristic for welding joints, and also affects the hardness distribution there. A higher hardness is always associated with HAZ where harder structures are formed (bainite and martensite). There are also higher internal stresses which additionally accelarated the SCC processes. This means that if the crack front has reached HAZ, the SCC process has rapidly accelarated because of mechanical factors. Microscopic observations proved that the leading mechanism of SCC in tested steel is based on "preexisting active path" but hydrogen assisted craking in the HAZ can not be neglected because of the hard structural constituents formed there. In tested specimens, the HAZ was relatively thin and such mechanism had a small share in the total SCC processes in this steel. The specimens did not fulfill the Brown's, formula for plain-strain conditions but according to (10) SCC always produces brittle fracture. The estimated K_{SCC} value is valid for this steel if the thickness of the constructional member is smaller than 15mm. Such a value (K_{SCC}) marked in Fig. 8 should be considered as an obligatory limit for engineering calculations of allowable stresses when the welded constructions will be exposed to NaCl solutions or marine atmosphere.

CONCLUSIONS

Some important conclusions based on experimental and theoretical data are as follows :

1. In spite of the general opinion that low-carbon steels are not significantly susceptible to SCC in water environments containing NaCl with a pH below 7, the presented results show that in welded areas such steels are highly susceptible to this type of corrosion.

2. Susceptibility of welded joints to SCC exposed to aerated 3.5% NaCl water solution is of the range (K_{SCC} / K_{IC}) = 0.72 (± 0.03) which belongs to the class of the high susceptibility (10).

3. The leading mechanism of SCC in welding joints belongs to "preexisting active path" type.

4. The main reason for the high susceptibility of tested weldments to SCC is due to the high level of different inhomogeneities and internal stresses introduced by the welding process. Such high levels of detrimental factors (from a SCC point of view), do not exist in the parent steel per se, and such steel can exhibit low sensitivity to SCC exposed to NaCl solution, but in a welded structure such an opinion is not correct.

5. It is necessary to underline that such important experiments should be repeated for a greater number of welded specimens with different shapes of joints and welding technologies.

6. The projects of salt-water installations, offshore platforms etc, should be checked for allowable stresses which must not exceed K_{ISCC} value for welding joints.

ACKNOWLEDGEMENT

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PRJ Vol 1, (January 1989); P. 11–16, 4 TABLES.

EVALUATION OF METHANOL BASED INDUSTRIES

A. Alem *

تقييم الصناعات القائمة على الميثانول

د . عبد العاطى العالم

تنتج الجماهيرية كميات ضخمة من مادة الميثانول تقدر بحوالى 4٪ من الطاقة العالمية لهذه المادة ، والميثانول يعتبر المادة الخام الرئيسية فى عديد من الصناعات الكيمائية ، والتى اهمها الفورمالدهايد وحامض الاسيتيك وكلوريد الميثيل وغيرها .. كما أنه من المؤكد استعماله كاضافة لبنزين السيارات بنسبة تتراوح من 3 ـ 5 ٪ بطريقة مباشرة أو غير مباشرة فى صورة مادة (MTBE) .

تهدف هذه الدراسة الى التعرض لطرق التقنية المختلفة لصناعة المواد المعتمدة على الميثانول ، واختيار الطاقة الانتاجية المثلى لكل صناعة باستخدام النماذج الرياضية وايجاد تكلفة الانتاج فى كل حالة مأخوذا فى الاعتبار قدرة الاسواق العالمية على استيعاب هذه المنتجات وتقديرات استيعاب السوق المحلى من الدراسات السابقة فى هذا المجال .

وقد تم التوصل الى أن افضل سعة لمصنع حامض الاسيتيك هى «40,000» طن سنويا ليحقق المصنع عائدا سنويا يبلغ 10٪ . ومع ان مصنع الفورمالدهايد يؤدى الى عائد سالب عند هذه السعة الانتاجية مما يستوجب تصميم المصنع بطاقة انتاجية لا تقل عن 45,000 طن سنويا ، ونظرا لأن السوق المحلى يستوعب كمية من هذه المادة فى المستقبل القريب فان الدراسة توصى بتنفيذه قبل حامض الاسيتيك ، والذى لا يوجد له استعمال فى المستقبل القريب بالجماهيرية . وقد درس مصنع الفورمالدهايد كوسيلة لزيادة الدخل القومى وكانت النتائج مشجعة ..

ABSTRACT

Jamahiriya produces about 4% of the total world capacity of methanol. It is expected that the world consumption of methanol will sharply increase in near future as a result of its direct and indirect use as a blend to motor gasoline leading to an anticipated higher prices. Mathematical models are used in this study to assess different technologies of different methanol - based products in order to optimize the uses of methanol in libya and to assess the variations of production capacities on the production cost. Productions of formaldehyde and acetic acid from methanol are evaluated to optimize several perturbations such as the capacity of each plant, the energy cost and the level of operations on the objective function ,. Enhancement ratio, pay-out period and rate of return on investment are calculated using the model to assess their sensitivity to the model's parameters. Acetic acid plant produces a rate of return of 10% at relatively small capacity of 40,000 tons/year. Formaldehyde plant has a negative rate of return at a similar capacity. Formaldehyde plant is feasible with minimum capacity of 45,000 tons/year as partial local utilization is projected. Evaluation of formaldehyde plant as a source of generating foreign currency leads to encouraging results.

INTRODUCTION

Oil and natural gas and their derivatives have traditionally been used as main energy sources worldwide . This situation is expected to continue for many decades to come. The major reasons are the availability and the financial considerations. Different technologies have been developed to optimize the processes searching for better economics. During practising these developments, many by-products are obtained as either side streams or kind of impurities to be separated. As a result many products are produced and used in different objectives such as inhibitors, additives, plasticizers etc.

Methanol is a basic petrochemical product obtained from natural gas . It is the starting point for many production chains and processes covering the three broad categories in petrochemical industry classifications, basic, intermediate and final products.

Methanol is the raw material for many petrochemical products such as formaldehyde (Adhesive industry), acetic acid, methyl chloride, chloroform etc. It is expected to be used directly in energy utilization including driving cars in near future. The increased processing ability and varying the products from a certain source-including methanol raises

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automatically the enhancement ratio and the value added component derived from that source. Payout period is also expected to be reduced sharply for the whole chain of industry based on that source leading to the improvement of economics including the rate of return on investment. Marketing strategies based on supply-demand balance is one of the major constraints to optimize the methanol production and its derivatives in any country. Joint venture is one of the forms to ease the marketing problem in case of tightly controlled world market for a certain product.

The world demand of methanol stands at 15 million metric tons per year. Libya produces about 4% of this capacity. World demand of the two major methanol derivatives formaldehyde and acetic acid-exceeds 19 and 6 millons metric tons per year, respectively.

TECHNOLOGY AND USES

Methanol

It is the basic feed-stock of the processess assessed in this study. Methanol is produced in Libya from methane. The favoured process to produce methanol is the intermediate pressure process (103 atm) at a temperature of 450-520°F, using copper oxide, aluminium oxide and zinc oxide as catalyst. The main uses of methanol is in the production for formaldehyde, acetic acid solvent and lately as fuel. The world supply-demand of methanol is encouraging. It is expected that the demand of methanol will sharply increase in near future.

The use of 3-5% of methanol as a blend to motor gasoline is investigated in many countries and results are comercially implemented. Shortages of methanol as a result will be expected. In small countries such as Libya, 60,000 tons of extra methanol is needed if the blend is approved. Production of formaldehyde and acetic acid will be affected due to the shortage of the raw materials available for the processes. As a result higher prices will be anticipated in future. Although new technologies based on other raw materials may be developed, it will take long time before the developed processes will be commercialized.

Formaldehyde

The main use of formaldehyde is in the resin industry. The chief use of urea-formaldehyde resins is as an adhesive in fibrous and granulated wood products. Melamine-formaldehyde resins are used as decorative laminates in furniture manufacture.

Formaldehyde is marketed in the form of acqueous solution containing 37% of dissolved formaldehyde gas. Small percentage of methanol is present to avoid polymerization during storage and transportation period. There are two well known processes to produce formaldehyde, metal oxide catalyst process and silver catalyst process. The selection of one of the two processes depends mainly on end uses rather than economical considerations. The metal oxide process is selected where molybdenum oxide-iron oxide catalyst are used at 5-10 psi and at a temperature of 600-700 °F. Methanol is used as a raw material with a rate of 1.18 ton per ton of pure formaldehyde produced. The catalyst is selected to balance thermally the endothermic dehydrogeneration with the exothermic oxidation. Summary of the assessment of formaldehyde plant is presented in table (1).

Table 1. Assessment of formaldehyde plant

Plant Capacity Thousand tons/year	30	45	57	72	90
Methanol needed Thousands tons/year	12.6	18.9	24	30.5	38
Cost of raw materials and catalyst	1.6	2.4	3.05	3.88	4.83
Fixed Capital Investment	15	18.8	21.4	24.3	27.6
Working Capital Investment	1.5	1.9	2.1	2.5	2.7
Enhacement Ratio :					
i) Excluding primary Energy Cost	2.83	2.83	2.83	2.82	2.82
ii) Including Energy Cost	2.62	2.62	2.6	2.6	2.6
Pay-out period	5.7	4.5	3.9	3.4	3
Rate of Return	0.56	-1.47	1.84	5.43	13.17

Acetic Acid

Acetic acid is prepared from methanol through the reaction with carbon monoxide. From material balance 0.58 ton of methanol is reacted with 0.61 ton of carbon monoxide to produce one ton of acetic acid. The energy required for the process is estimated at 0.3 fuel oil equivalent ton per ton of the product. The reaction takes place at 500 psi and a temperature of 390 °F. Rhodium is used as a catalyst. The main uses of acetic acid is in the production of acetic anhydride, vinyl acetate and various acetate esters. Assessment of acetic acid plant at different capacities is listed in table (2).

Table 2. Assessment of acetic acid plant

Plant Capacity Thousand tons/year	39	48	77	91
Methanol needed Thousands tons/year	24	30	48	57
Cost of raw materials	2.9	3.6	5.8	10.9
Fixed Capital Investment	20.7	24	33.4	37
Working Capital Investment	4.3	5.9	8.1	9.4
Enhacement Ratio :				
i) Excluding Primary Energy Cost**	2.6	2.6	2.6	2.6
ii) Including energy Cost	2.3	2.3	2.3	2.3
Rate of Return	10	16	33	41

THE MODEL AND CALCULATIONS

Methanol-based petrochemical industry is highly developed with wide variations in technological processes. It is well intergrated industry with many variables that cause change by orderly perturbations from the usual practice of producing methanol. Different technologies of different methanol-based products are assessed using the developed model in an attempt to optimize the production cost. The model is used to evaluate 9 cases. The concentration is based on three different uses of methanol, acetic acid, formaldehyde and gasoline additives. Capacity of each industry is varied in the model with two major constraints the total productions of methanol and the percentage of methanol used in the gasoline-methanol blend.

The different cases in this work are analysed to show the effect of several perturbations such as the capacity of each industry, the energy cost and surplus on the enhancement ratio and the payout period. The surplus is defined as the production capacity of a certain product minus the demand.

It is difficult to treat the surplus as a factor in the model due to the large fluctuations and unstability of petrochemical products in the world markets. This problem is solved through the treatment of surplus as a heating value product. The objective function in this work is selected to represent the total production cost. The optimization of the objective function is subject to the constraint of the limited capacity.

Enhacement ratio and pay-out period together with the rate of return on investment are calculated using the model to assess their sensitivity. The model is represented by the following equation (1):

$$y = \sum_{k=1}^{N} h_k f_k + \sum_{j=1}^{M} H_j (D_j - R_j) + \sum_{x=1}^{n} (L_x \times x_x)$$

Where

y is the total production cost of the desired product.

$h_k f_k$ represents the cost of raw materials.

H_j is a chemical price.

$(D_j - R_j)$ represents the surplus production which is evaluated in the model as a heating value instead of chemical value. By products are considered as credits.

L_x represents the investment, labour, additives, catalysts and utilities cost.

R_j is the product demand.

X_x is the level of operations which have to be varied to optimize the total production cost.

D_j represents the production capacity.

The enhancement ratio (ER) is calculated using the following equation:

$$ER = (D_j H_j) \Big/ \left(\sum_{k=1}^{N} h_k f_k + E \right)$$

where E is the primary energy cost which is evaluated relatively to fuel oil equivalent ton per ton produced.

The pay-out period is calculated for each industry (methanol, formaldehyde and acetic acid) using the cost index and literature (2) value for the base case.

The fixed capital investment is calculated for each industry (methanol, formaldehyde and acetic acid) using the cost index and literature (2) value for the base case.

Adjustment of the capacity is performed using the following equation (2):

$$C_1 / C_2 = (Q_1 / Q_2)^q$$

Where C_1 is the fixed capital of the base case plant with a capacity equal to Q_1. C_2 is the fixed capital of the same plant at the same year but at a capacity equal to Q_2. And q is a constant.

The same procedure is followed to evaluate the battery limit (B.L.) cost. The cost is then evaluated based to the Libyan market, a location factor of 2 is used for this purpose.

The following constraints are considered in the model :

1. The total capacities of methanol production is 600,000 tons/year.
   This is treated as a supply limitation where
   $f_i < S_i$ (Where S_i = 600,000 tons/year)

2. The process capacity is limited :
   $x_i < Q_i$
   (Where Q_i is the maximum capacity which can be absorbed for Libyan formaldehyde in world market)

3. Evaluation of local and foreign market of a certain production D creates a demand constraint :

   $R_j < D_j$

4. Maintenance is considered as a percentage of 3% of battery limit per year, while labour is based on the rate of 2.5 Libyan dinars per man hour, Laboratory service is charged at 25% of operating labour.

5. Electricity is charged at 0.39 kwh/lb, process water at 0.1482 gal/lb and cooling water at 32.55 gal/lb. with a cost of 0037 cent/lb. The electricity is evaluated at 8.1 cent/kwh while the process water is charged at 0.45 cent/lb.

6. The plant overhead is charged at 75% of total labour, insurance is treated as 2% of fixed capital per year. The depreciation is evaluated at 10% / year (linear method).

RESULTS AND CALCULATIONS

Methanol is considered as one of the most basic petro-chemical compounds. Large industries depend on methanol as a raw material. Although there is a glut of methanol worldwide at present, the situation will differ completely when oxygenated alcohols will be used with certain percentages in motor gasoline. This direction seems to be implemented in near future. Shortage of methanol and its derivatives mainly acetic and formaldehyde will be faced and this situation will obviously lead to higher prices for these products. This study is based on the production of formaldehyde and acetic acid in Libya. Total capital investments are calculated for different plant capacities. Enhancement ratio including and excluding primary energy cost and pay-out period are evaluated. Rate of return is obtained for each capacity of each plant. The results are summerized in tables 1 & 2. It is obvious from these tables that better economics will be achieved from larger capacity. However, supply/demand issue worldwide put a limit on the capacity. Negative rate of return is expected when the capacity is lower than 50,000 tons/year of formaldehyde. The maximum rate of return is achieved with a capacity of 90,000 tons/year of 37% formaldehyde. This plant will consume 38,000 tons/year of methanol. Results listed in table (2) show that acetic acid plant is more attractive if market is available. The production cost of acetic acid will be $ 338/ton at a capacity of 40,000 tons/year. Rate of return is 10% at this relatively small capacity.

However, development of local market utilizing formaldehyde in near future makes it more favourable than acetic acid, although the later has better economics. Local market is expected to be developed locally to produce urea-formaldehyde, melamine formaldehyde and phenol-formaldehyde resins. Ten thousands to 16,000 tons/year may be consumed locally in near future. Assessment of formaldehyde plant from the point of saving foreign currency is considered in this study. Two levels of formaldehyde local needs are evaluated. The amount of revenue associated with import elimination of formaldehyde is considered as positive foreign currency saving. It is balanced against the payments abroad required to cover the cost of maintenance, expatriate labour, catalyst etc. The saving in foreign currency of the formaldehyde plant is indicated in tables (3-4) for two different capacities 30,000 and 45,000 tons/year.

The local demand of formaldehyde is estimated at 10,000 and 16,500 tons/year in 1990(3).

SUMMARY AND CONCLUSIONS

Capital investment, enhacement ratio, pay-out period and rate of return are calculated for major methanol-based industries with different capacities. From the results of all cases studied, it is evident that local markets should be developed for the integration of these products. Although international market is hardly to penetrate in present time, future is bright for the products depending on methanol as a feedstock. This situation will be developed in near future because of the strong possibility of using methanol as a blend in motor gasoline. Production of formaldehyde and acetic acid in Libya, if any should not exceed 5% of the total production capacity of methanol in Libya due to supply-demand limitations. This constraint represents severe limitations on the freedom to select optimal production cost. Although one of the solution to this constraint comes through joint venture agreement, this is not always the best and open alternative. The economics of the two major

Table 3. Total foreign currency revenues

CASE 1. Formaldehyde plant 30,000 tons capacity with local demand of 10,000 tons/year

YEAR	FOREIGN CURRENCY EXPENDITURE ON PLANT	FOREIGN CURRENCY EXPENDITURE ON WORKING CAPITAL	FOREIGN CURRENCY EXPENDITURE ON PRODUCTION	IMPORT VALUE	FOREIGN CURRENCY REVENUES FROM EXPORT	FOREIGN NET CURRENCY SAVINGS/ REVENUES	FOREIGN CURRENCY GENERATED BY RAW MATERIAL	OVERALL NET
-2	-4.500				-	-4.500		
-1	-5.251				-	-5.251		
0	-5.251	-0.450			-	-5.251		
1		-0.450	-1.164	+1.815	+1.337	+1.538		
2		-0.450	-1.204	+2.0	+1.871	+2.779		
3		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
4		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
5		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
6		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
7		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
8		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
9		-0.450	1.204	+2.0	+3.6	+3.946	-1.512	+2.434
10		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
11		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
12		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
13		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
14		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
15		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434

Table 4.Total foreign currency revenues

CASE I. Formaldehyde plant 45,000 tons capacity with local demand of 10,000 tons/year

YEAR	FOREIGN CURRENCY EXPENDITURE ON PLANT	FOREIGN CURRENCY EXPENDITURE ON WORKING CAPITAL	FOREIGN CURRENCY EXPENDITURE ON PRODUCTION	IMPORT VALUE	FOREIGN CURRENCY REVENUES FROM EXPORT	FOREIGN NET CURRENCY SAVINGS/ REVENUES	FORIEGN CURRENCY GENERATED BY RAW MATERIAL	OVERALL NET
-2	-5.625				-	-5.625		
-1	-6.5625				-	-6.5625		
0	-6.5625				-	-6.5625		
1		-0.563	-1.164	+1.815	+1.337	+1.425		
2		-0.563	-1.183	+2.541	+1.871	+2.666		
3		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
4		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
5		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
6		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
7		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
8		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
9		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
10		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
11		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
12		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
13		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
14		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
15		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801

processes to manufacture formaldehyde is not a decisive factor. The ratio of production cost of formaldehyde using silver catalyst process is 1.02 times the molybdenum catalyst. Using 5% of the capacity of methanol in gasoline production is attractive economically if technical problems are solved. Present local and world supply-demand does not justify building new plants for the manufacture of either formaldehyde or acetic acid. However, formaldehyde plant is feasible with minimun capacity of 45,000 tons/year as partial local utilization is projected. Formaldehyde plant is evaluated as a source of generating foreign currency with positive results, Total foreign currency revenues are calculated at different capacities of formaldehyde plant including 30,000, 45,000 and 57,000 tons/year. The calculations are performed at two different levels of local demand at 10,000 and 16,500 tons/year. The overall net is maximized at 8,8 million dollars at a capacity of 45,000 tons/year with a local demand of 10,000 tons/year. Sample calculations are presented in tables (3) and (4). This work should continue to evaluate the sensitivity of these projects for fluctuations in world market prices.

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HYDROCARBON HABITAT IN THE SIRTE BASIN NORTHERN LIBYA

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دراسة صخور المصدر الهيدروكربونية فى حوض سرت

مصطفى العلمى ، سلامة رحومة ، د . أ . بات

القت هذه الدراسة الضوء على اهم صخور المصدر بحوض سرت وهى تكوين سرت الطفلى بتحديد سحناته الرسوبية والبيئية وتقييم وضعه الطبقى والتركيبى والذى تمثل فى جملتها العوامل المتحكمة فى توليد النفط وهجرته وتجمعه فى حوض سرت .

وتم اعتمادا على ربط المعلومات الجيولوجية بالبيانات الجيوكيميائية تقييم تكوين سرت تقييما اقليميا يغطى مختلف مقاطع الحوض وذلك لغرض استنتاج طاقته المولده للمواد الهيدروكربونية مما يساعد فى عمليات الاستكشاف مستقبلا . كما تم توضيح المناطق الرئيسية المولدة للنفط والمولدة للغاز . هذا وتعتبر جميع المكامن النفطية القريبة من صخور المصدر مهمة وتقل درجة اهميتها بزيادة المسافة بين المكمن وهذه المناطق الرئيسية ويعتقد هنا أن اغلب النفط فى حقول حوض سرت كانت قد تولدت من صخور تكوين سرت الطفلى ويستثنى من ذلك نفط حقول ابو الطفل والسرير وأمال والحقول الواقعة بعقد امتياز 80 حيث يعتقد أن النفط هناك تولد من صخور قارية .

ABSTRACT

The Oil-Prone organic facies II of the marine Upper Cretaceous (mainly Campanian) Sirte Shale, including its micritic facies, developed in the eastern Sirte Basin, occupies the central part of the "Oil generative depressions", where the depth of burial is sufficient for thermal maturation. This is based upon a large amount of geochemical data collected over the last years by the Petroleum Research Centre .

The combination of favourable organic facies and maturation level of the Sirte Shale defines the areas of major oil generation in the Zella Trough, the Marada Trough (also called the Hagfa Trough) and the Agedabia Trough. The giant oil fields tend to occur within short distance migration range from these oil-generative depressions.

The evolution of the various segments of the Sirte Basin, in terms of their remaining potential hydrocarbon prospects, can be made by employing conventional methods of petroleum geology in conjunction with precise knowledge of where and when oil was generated in the various segments of the basin.

INTRODUCTION

The Sirte Basin with its series of northwest-southeast trending horst and graben blocks forms an important structural province of Northern Libya (Figure 1). It is a prolific oil producing basin and is considered to contain more than one adequately mature source rock. Reports of petroleum geochemical studies so far remain unpublished (e.g. Robertson Res. Int. 1979) and have been largely restricted to each operator's area of interest. However, the available petroleum geochemical studies do not throw sufficient light on the mode of formation and stratigraphical position of these effective hydrocarbon sources in the basin as a whole. An attempt has therefore been made to consolidate the available source rock data of 88 wells covering the Sirte Basin (Figure 2) and to integrate the data with the results of geochemical investigations of 57 oil samples in order to identify the regional source-bed occurences. The outcome is also used to assess the potential hydrocarbon prospects of the various parts of the Basin.

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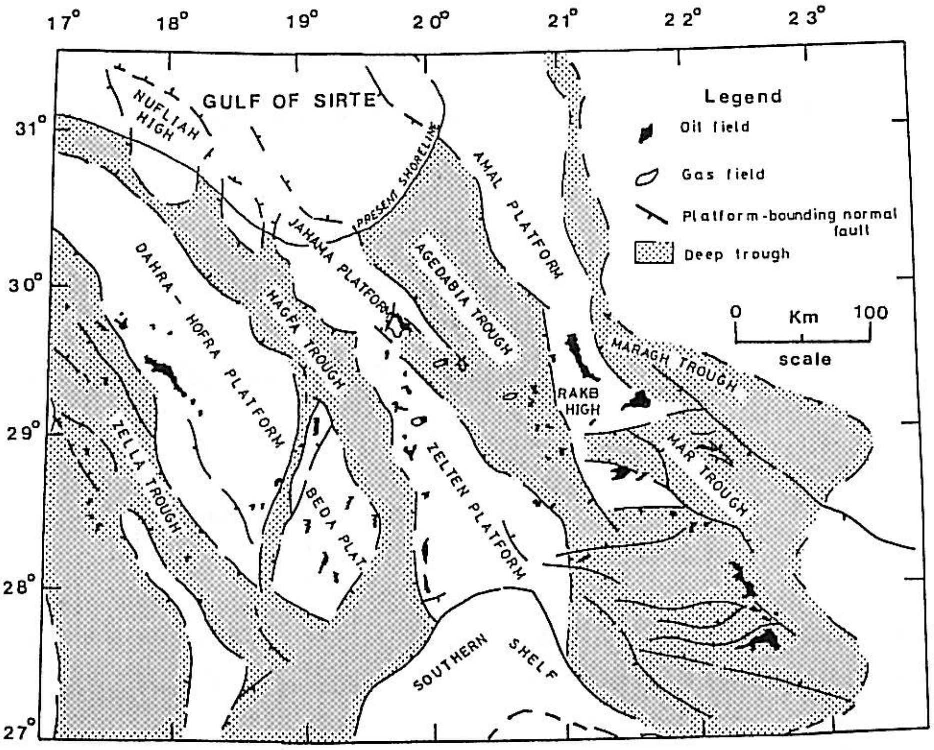

FIG. 1. Major tectonic elements of Sirte Basin, Libya. (After El-Mouzughi and Taleb, 1981)

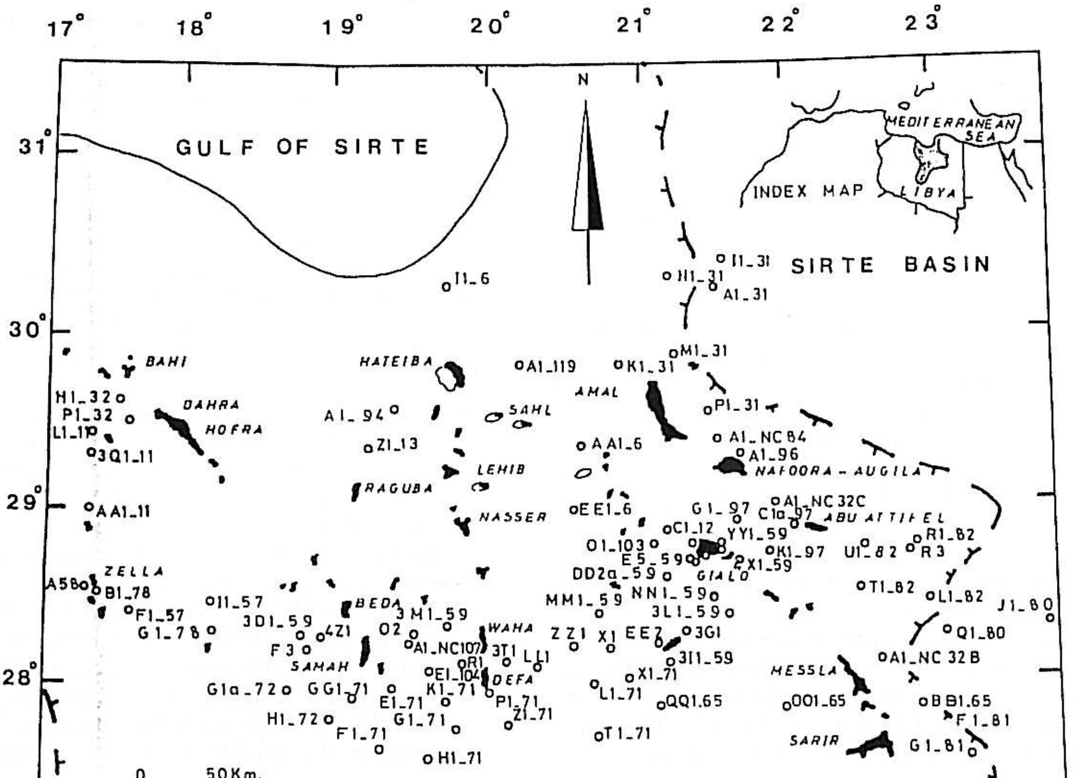

FIG. 2. Location map showing the wells of source rock study.

The attempt here involves studies of richness, maturation, oil to source-rock correlation, time of oil generation and migration. Stratigraphic principle and organic facies concepts due to Demaison et al (1983) are additionally employed. The marine Upper Cretaceous (mainly Campanian) Sirte shale is concluded to possibly constitute the prime source-rock for hydrocarbon generation and accumulation because of the favourable depositional environment, organic carbon contents, stratigraphic and structural setting characterising the formation.

The Sirte shale is a widely distributed stratigraphic unit of the Basin. It occurs dominantly as a laminated, carbonaceous, non-bioturbated sequence of dark grey to mainly dark brown shales grading into shaly limestone at the lower part. In the eastern Sirte Basin, however, the lower part of the shale passes into a calcareous facies, namely the Tagrifet limestone (Barr and weegar, 1972). In relation to this region. Sirte Shale is used as restricted to the upper shale sequence. Williams (1968) referred to it as Rakb Shale. In so far as the source-rock evaluation attempted in the present work is concerned, the Sirte Shale (Sensu stricto) includes the whole sequence of the formation and its equivalent, the Tagrifet Limestone.

In general, the bulk of the oil is derived from the Sirte Shale. Locally, however, in the eastern Sirte Basin, oil is also derived from source rocks deposited under paralic to continental environments that dominated in the Turonian and Lower Cretaceous times. Paleogeographic distribution of the source beds for these oils which have significantly high content of wax is little known.

The traps within or adjacent to generative troughs are important as exploration targets. This is because of the occurence of the source rock, the migration distances which are likely to be short or moderate and the conductive geologic setting for the entrapment of hydrocarbons, all resulting from the horst-graben tectonic fabric present in the region. In the present work, the model of hydrocarbon occurence and entrapment is studied based on the examination of the geological and petroleum geochemical characteristics to finally demarcate the effective hydrocarbon source rocks in the Sirte Basin.

REGIONAL SETTING

The Sirte Basin persisted from the Silurian until the Jurassic as an extensive uplifted tract with NW-SE orientation consequent upon the trend of Caledonian movements (Massa, 1984). The eroded arch was rifted to form the Sirte Basin aided by tensional movements in the Late jurassic. Sedimentation began in Early Cretaceous time when nonmarine to parallic sediments of the Nubian formation started to accumulate in small grabens.

Full scale rifting and block faulting took place in Upper Cretaceous time. This lead to marine transgression and associated subtle facies changes across the lines of contemporaneous faults. Difficulties of nomenclature exist obviously due to the abrupt changes in depositional conditions.

This main NW-SE synclinal trough remained active during the tertiary as the Basin continued to subside. In general, all the structural highs came to be masked by the later, Tertiary sedimentation and by mid Paleocene time, the region developed into a unique Basin (Roberts, 1970). Intense tectonic activity returned again during the Oligocene and Early Miocene bringing about the regional uplift. Towards the end of Middle Miocene the present onshore part of the Sirte Basin had emerged.

DEPOSITIONAL ENVIRONMENTS

The unique basin geometry of the Sirte Basin with opening into the Mediterranean indicate marine transgression to have taken place from the north during the Campanian time (Figure 3). The northerly open marine conditions permitting active intermixing of water masses led to oxigenation environment. Presence of planktonic foraminifera throughout the formation in the northern Sirte Basin together with benthonic foraminifera (Barr and Weeger, 1972) corroborates the indication of open marine and outer neritic environment. The paleoceanographic factor is suggestive of minimum possibilities for petroleum source bed deposition (Demison and Moore, 1980).

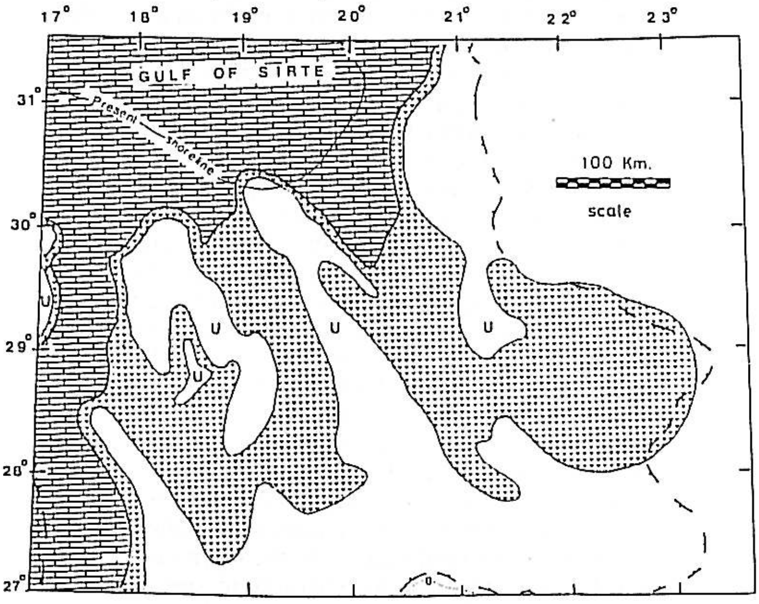

FIG. 3. Paleogeographic map of transgressive Turonian deposits, as based on the analysis of Etel evaporites and its basinward equivalent, Sirte Basin, Libya.

Longitudinal trough areas, however, gave rise to restricted marine environments further into the interior of the Basin. These formed tracts of inactive mixing of water masses with tendency to development of stagnant waters. Barr and weeger (1972) reported that the lower part of the Sirte Shale, barring the northern part of the Basin, contain small sized bulimines. At the same time, the upper parts of the sequence abound in both planktonic and benthonic foraminifera. The most ubiquitons of the benthonic foraminiferal species appears to be the Siphogeneranoides Cretacea. The most conspicuous of the small size bulimines in the lower part of the Sirte Shale is the Bulimina Prolixa (Cushman and Parker, 1947) which points to the prevalence of a restricted marine environment. Such environments lead to reducing (depletion of oxygen) conditions. It indicates the tendency towards development of stagnant waters as it becomes a zone of insufficient mixing of water masses (Demaison et, 1983). Moreover, the bulimines are known to tolerate such stressed environments of stagnant conditions with low level oxygen (Haynes, 1981). Consequently, they buildup small, smooth and thin skeletons vis-a-vis the normal marine milieu. Higher up in the formation, a tendency towards amelioration of marine reducing environment occurs as indicated by the presence of both planktonic and benthonic foraminifera.

The Tagrifet Limestone (lateral) facies equivalent of the lower part of the Sirte Shale) is located in the eastern part of the basin. It has been described in detail as the Rakb Carbonates by Williams (1968) who concluded that the upper micritic unit of the Rakb Carbonates was deposited in a low energy, open sea environment in water depths of about 34-45 meters. It probably forms some of the source beds, while its lower unit in the Augila-Nafoora Fields is considered as a reservoir rock deposited in shallow marine environment (epineritic) as the sea transgressed across the basement highs. The Tagrifet Limestone is generally a dark brown, oil-saturated and argillaceous planktonic micrite containing a few very fine grains of dolomite and pyrite. Traces of phosphatic grains are scattered throughout. While the biofacies is recognized by Globotruncana and Heterohelix faunas filled with calcite or pyrite, non bioturbated and the benthic fauna is sparse and consists solely of rare Incoeramus sp. fragments. The lithology and fauna may be considered as evidence of an oxygen-depleated, low energy and shallow marine basin which had only access to the open ocean in the north where the oceanic currents in surface waters probably raised the number of planktonics.

It is likely that during sedimentation of the Sirte Shale and its equivalent rocks there was continuity in the growth of tectonic structure into horst-graben fabric in a shallow marine basin. A great deal of subsidence and transgression may have taken place alongside the tectonic develoment. The flow of surface currents was persistantly towards the Basin (positive input) which may have caused continual supply and concentration of nutrients (phosphates and nitrates). In addition, the plant nutrients such as phosphates and nitrates were carried into the seas in the grabens by fluvial drainage systems. These systems transported solutes leached from soil in the horsts to the grabens. Presence of phosphate nodules in Sirte Shale evidences the possibility.

The mineral nutrients in the presence of light lead to prolific primary biologic productivity resulting in the depleation of oxygen. The semi-enclosed seas confined to the grabens possibily promoted water stratification to increase the oxygen depleation. Evidence of anoxic sedimentation associated with continual supply of nutrients is found in the Sirte Shale in the form of laminations, attainment of brownish black colour presence of phosphate nodules and pyritic-concentrations, non-bioturbated sequence and finally by general absence of macrofossils. These features are apparent in the Sirte Shale of the type section encountered in well 02-59.

In conclusion it is possible to extend the source bed depositional model of silled basin reinforced by transgression to the basin during the period of deposition of the Sirte Shale.

SOURCE BED EVALUATION

The quantity of organic material in a rock, the oil generative quality of the organic material determined by the type of the organic matter such as the algal, amorphous, woody and other contents each having a different petroleum potential and the thermal maturity of the kerogen (solid organic substance transforming to hydrocarbons under given subsurface temperature and geologic time) form the factors which govern the oil source capacity of a sedimentary rock (Waples, 1980). It is also mentioned by Waples (1980) that many workers (viz. Hunt, 1972; Welte, 1965 and others) have been concerned with the concentration of organic carbon in source beds and their implication to oil source capacity. Waples (1980), also, stated that according to Hunt (1972) the organic carbon content of an average shale to be around 1% and the quantity factor to have unit (1.0) value.

The maximum thickness of Sirte Shale, with organic carbon content of oil potential exceeding 1%, occurs in the central parts of the troughs (Figure 4). Amorphous variety of kerogen predominates in these parts. Sirte Shale together with the micritic facies of the Tagrifet limestone containing more than 1% of organic carbon is found in the Agedabia Trough with a thickness of about 2500 feet. In the Zella Trough and Marada Trough, the thickness is over 1250 feet. In the Kotla Trough, the thickness is over 1000 feet. The organic carbon content is seen to reach a value of more than 5% within some intervals of the Sirte Shale. Such a section is encountered, for example, in the well 3M1-59 penetrating the depocenter of the Hagfa Trough.

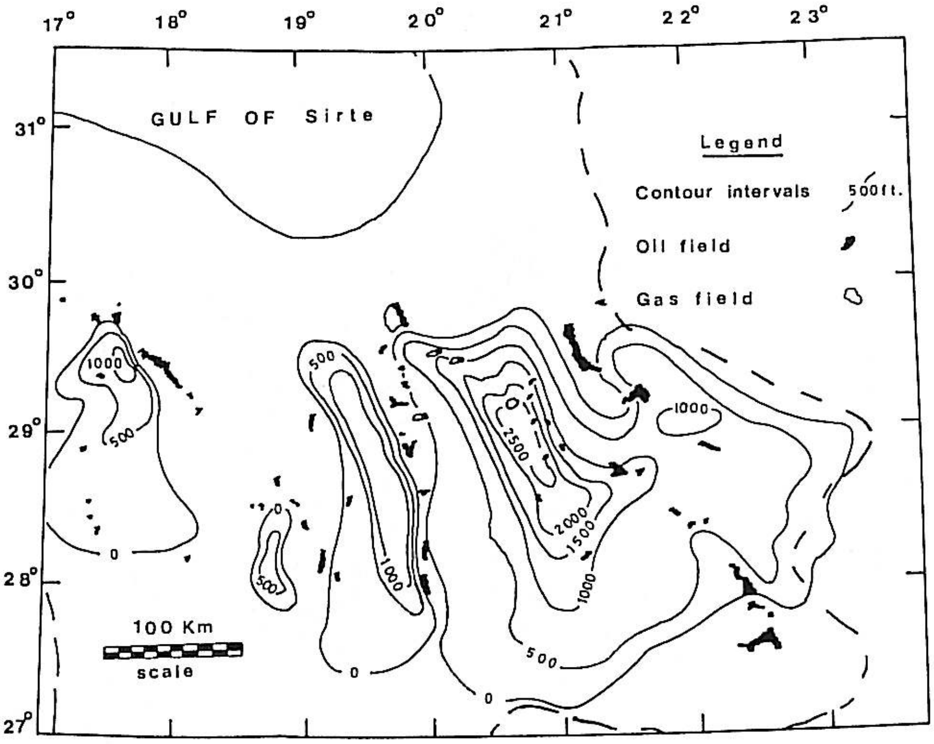

FIG. 4. Thickness of Sirte shale with over 1% organic carbon.

Carbon isotope data for the bulk of the Sirte Shale kerogen samples fall in a broad group with peak alkaline and aromatic hydrocabon fractions of – 29‰ and – 28‰, respectively. These percentages are indicative of strong terrestrial influence in the organic matter accumulations. Also the gas chromatoraph and mass fragmentograph data show relative abundance of steranes and re-arranged sterans to support the above indication. In the basin depocenters located away from the shoreline, however, the triterpanes are relatively more abundant. The carbon isotopes of the kerogene are seen to be slightly heavier to suggest significant algal influence in the constitution of the kerogen. Microscopic study shows that the type of organic matter is almost amorphous and herbaceous and that the algal fractions increase towards the depocenters of the troughs which is consistent with the other indications. The hydrogen index (80 to 480) and the pyrolysis G.C. data, given in table, emphasise the gas-prone to oil-prone gradation the above results invariably show.

Based on the data of pyrolysis G.C. and the type of kerogen as well as on the known geological history of the basin and by extending the organic facies concept of Demaison et al (1983), the distribution of various organic facies of Sirte Shale mapped for the region is presented in Figure 5. The map clearly brings out the non-source facies (type IV) prevalent in the area close to the horsts. The facies is inferred to have been deposited in oxic waters which existed in the shelf flanks as well as in the northern part of the basin. The situation is also characteristic of the western part of the Zella Trough (Tethys Sea). The oxic waters may have resulted from the replenishment of the oxygen under open marine conditions.

The facies is seen to grade from gas-prone (type III) to oil-prone (type II) towards the central part of the graben system. Strongly oil-prone (type I) facies is not found within the Sirte Shale sequence anywhere in the Basin. This feature signifies the possible prevalance of sub-oxic followed by protracted anoxic conditions obtained because of increasing water depths away fom the shoreline. Higher sedimentation rates towards the grabens combined with possible lower influence of terrigineous sources of organic matter may have additionally contributed to the observed situation.

The degree of maturation of kerogen within the Sirte Basin has been estimated as part of the present work from vitrinite refectances and spore coloration data using samples from 88 wells. Figure 6 synthesises the results and shows the presence of six major mature areas in the Basin as far as the Sirte Shale is concerned. These are located in the depocenters of Zella, Marada (Hagfa), Kotla, Agedabia, El-Hameimat (Mar) and Al-Quineen Troughs. The significant levels of oil generation in these areas required burial depths of the order of 10,000 to 11,500 feet. Minor oil generation in the region occured from good quality organic matter in the Sirte Shale and its lateral facies equivalents at depths less than 16000 feet and located between the wells EE 1-6 and AA1-6. Major gas-generation can therefore be anticipated in the corresponding region. Thermal

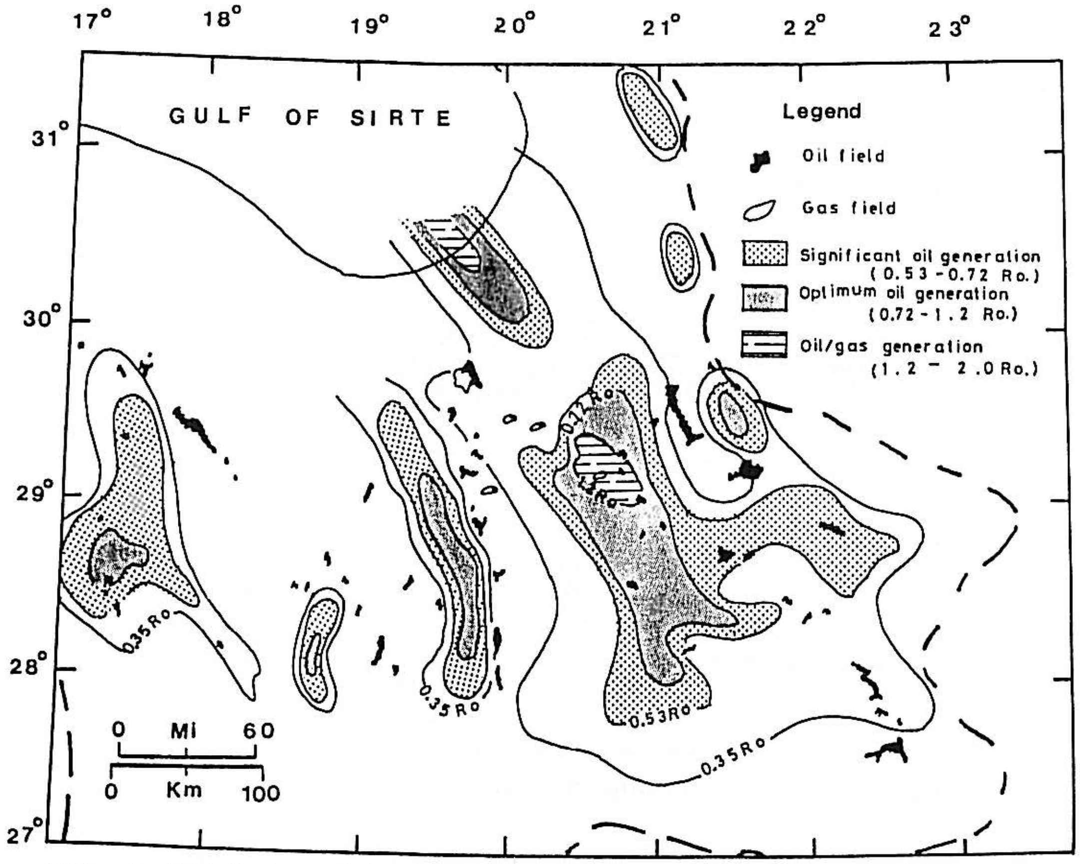

FIG. 5. Distribution of the organic facies, Sirte Shale, Sirte Basin.

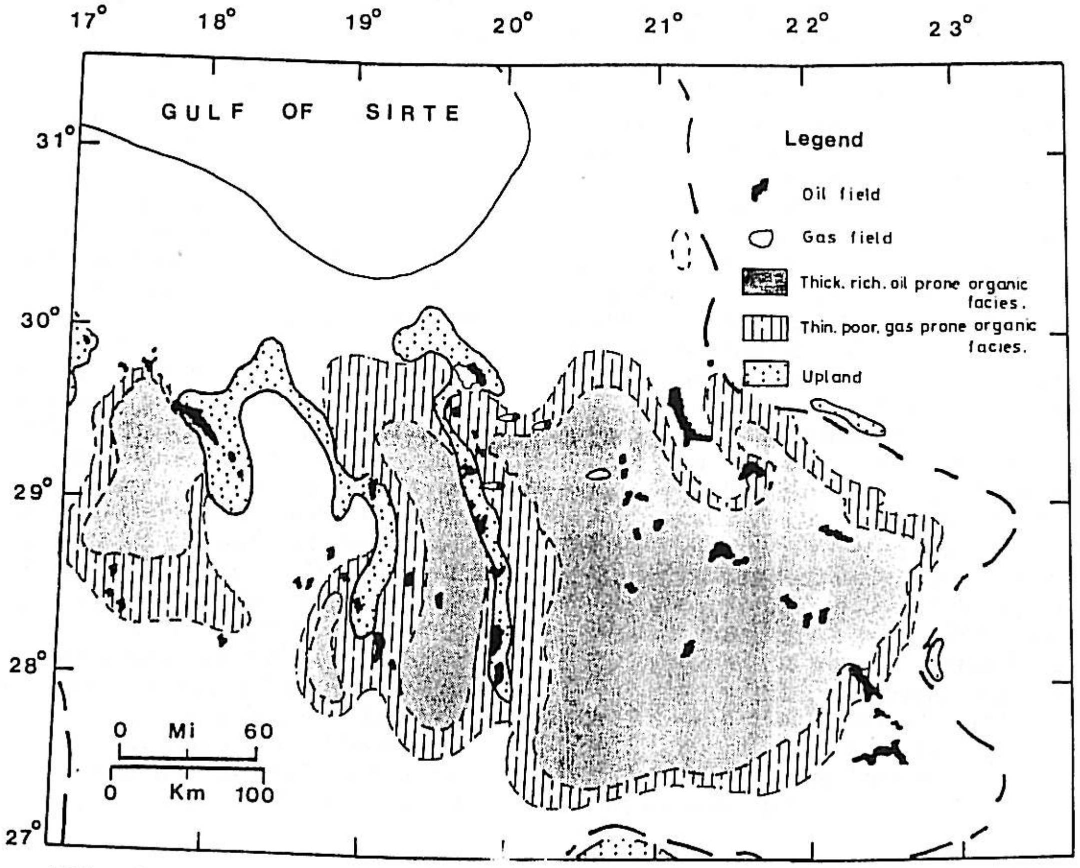

FIG. 6. Thermal maturation levels, Sirte Shale, Sirte Basin.

maturation has also been studied following Lopatin's method of Time Temperature Index (TTI) in assessing the possibility.

The combination of favourable organic facies and maturation levels enabled the demarcation of areas of major oil generation in the Sirte Basin (See Figure 7). The troughs in the Sirte Basin are seen to possess Sirte Shale deposits capable of generating major amounts of oil. In the shelf flank areas and south of approximately the latitude 28°N, however, the shale is characterised by the presence of immature and poor organic facies. The Sirte shale north of latitude 30°N again is likely to be in mature condition in the trough, but impoverished in organic matter to be oil-prone.

OIL TO SOURCE ROCK CORRELATION

A large number of possible source rocks have been identified in the Sirte Basin. Correlation data of 57 crude oil samples to their parent source rock in 88 wells as part of the source rock study attempted involved only the potentially effective source rock for oil.

The carbon isotope data for the bulk of oil samples is summarised in Figure 8. It shows two broad groups with peak values around – 28.5‰and – 27.5‰for parraffin-naphthanes and aromatic hydrocabon fractions, respectively. The carbon isotope of the Sirte Shale Kerogen is slightly less negative compared to

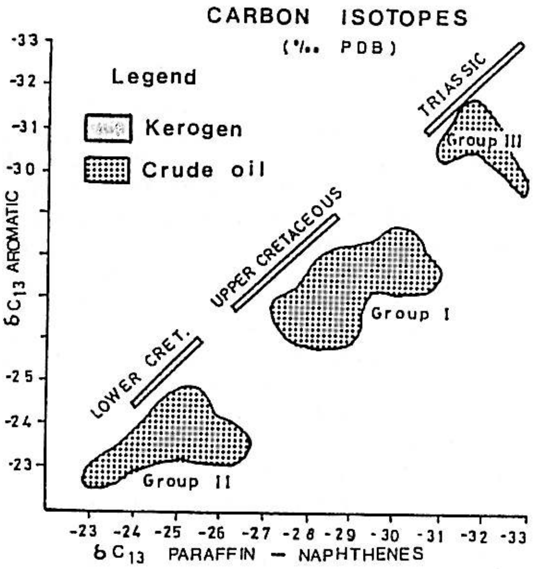

FIG. 8. Oil-source rock correlation based on carbon isotope.

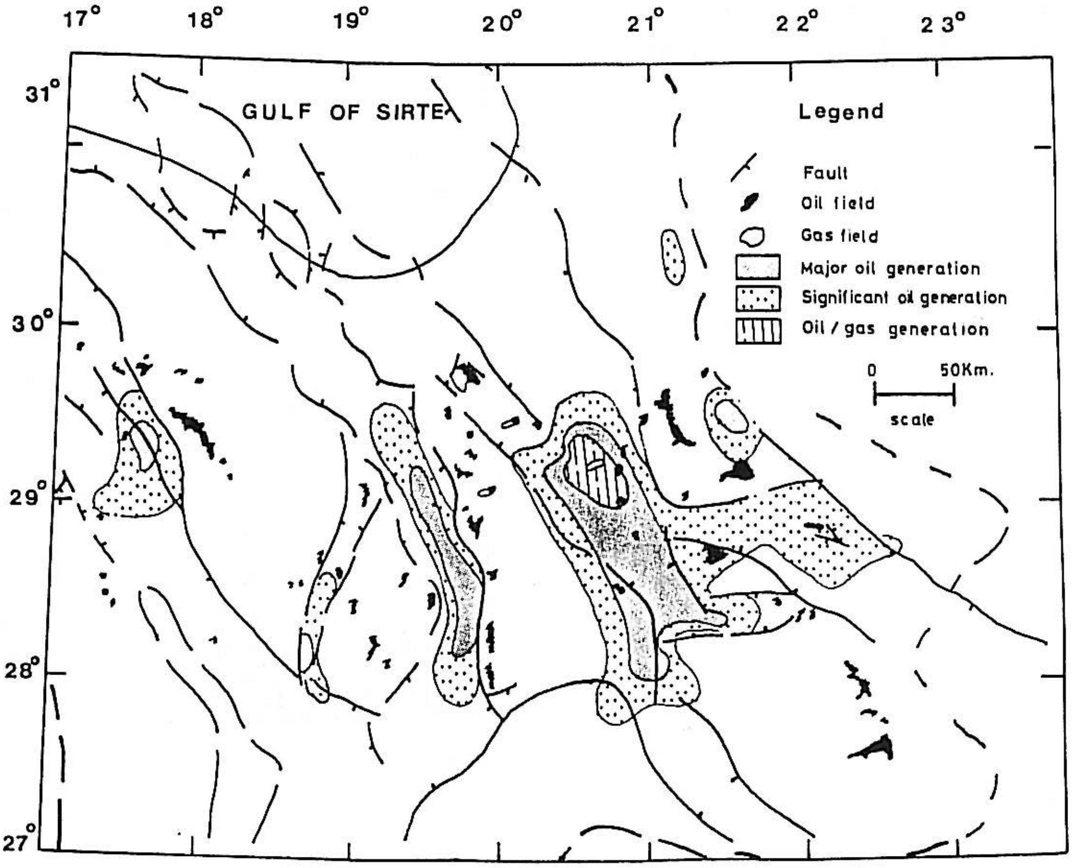

FIG. 7. Areas of major oil generation. Sirte Shale, Sirte Basin.

these peak values which points to terrestrial material input in the organic matter deposited under marine reducing environment. Variations in the carbon isotope fraction is probably associated with changes in the proportion of algal material input which increases towards the depocenters away from the shoreline.

In addition, there are source oils drawn from the southeast of the Sirte Basin which are isotopically heavier (by about – 23 to – 26%) and are distinct in other characteristics as well. The corresponding wells are EE2-59, JJ1-65, SI1-59, Abu Attifel, 0-80 Sarir and UUU 1-59. The crudes from these sites are waxy and appear to have affinity to the lower Cretaceous Shales and/or Etel Evaporites (Torounian Age). These oils of marked heavier isotopic values may have been derived from an algal source with significant terrestrial component and probably deposited in a lagoonal/lacustrine environment.

The oils in the Amal Field are isotopically distinct compared to the other crudes with values around – 31‰.They bear similarity to the source rock which is identified within the Triassic sediments in the well A1-96 near this field. The isotope values indicate association with land plant material deposited in a highly reducing environment.

The polycylic alkane analysis strengthens the results of carbon isotope ratio estimations. The bulk of the oil generated from the Sirte Shale exhibits relative similarity with its source rock judged on the basis of relative abundances of steranes and rearranged storanes. Figure 9 illustrates this feature indicative of land plant material input. The striped triterpanes in the figure points to significant algal component deposited under marine reducing environment. The oils possibly generated from the lower cretaceous shales and/or Etel evaporites are characterised by relative abundance of triterpanes compared to that of steranes and re-arranged steranes. This feature suggests that special species of algal material dominates the organic material that may have been deposited in lagoonal/lacustrine environment with significant terrestrial component input. These oils are also waxy (to about 25%) and have high proportion of C$_{20}$ + normal Paraffins bearing a similarity to the Nubian Shale sediments and/or Etel evaporites.

Sterane and triterpane analysis of oil from F1-31 shows that it is related to the Amal Crude. The crude is distinctly different compared to the first and second groups bearing affinity to Triassic sediments. Also the use of chromatograms to distinguish between crude oils and their parent source rocks point out that there are three groups of oil as forthcomes from Figure 10 derived from three different sources. The corresponding formations are the Upper Cretaceous Sirte Shale, the Lower Cretaceous Nubian Shale and the Triassic Shale.

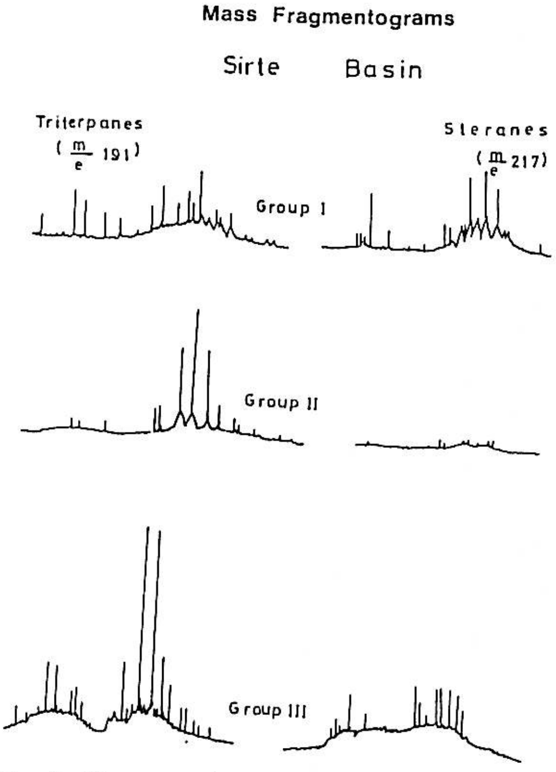

FIG. 9. Steranes-triterpanes correlation of oil groups in Sirte Basin.

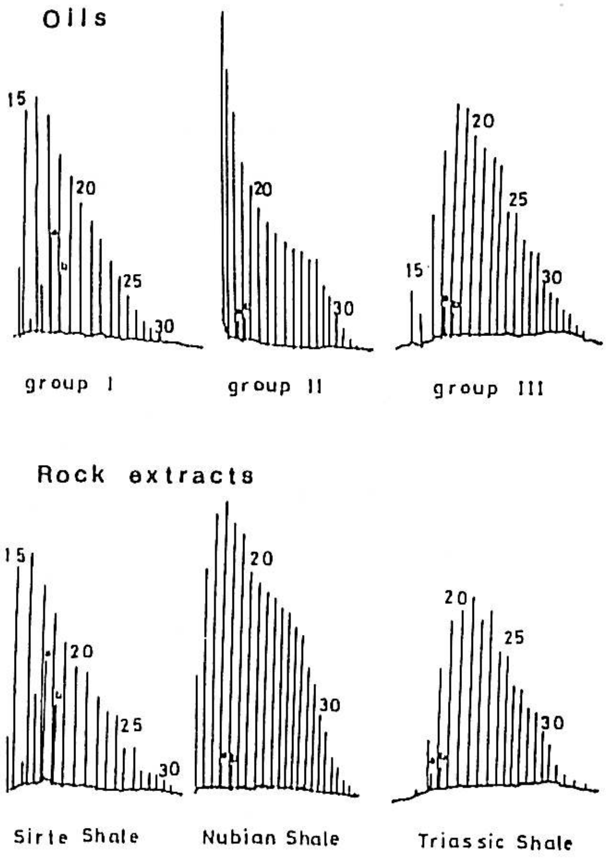

FIG. 10. C$_{15}$ + Paraffin-Naphthenes correlation of oil and rock extrects , Sirte Basin.

Geographic distribution of the oil groups is presented in Figure 11. It shows the relative extensive distribution of the first group with source in the Sirte Shale. The oils from Nubian Shale source rock are limited in occurence to the southeastern Sirte Basin and the oils derived from the Triassic source rock are found only in Amal, F1-31 and A1-96 well sites.

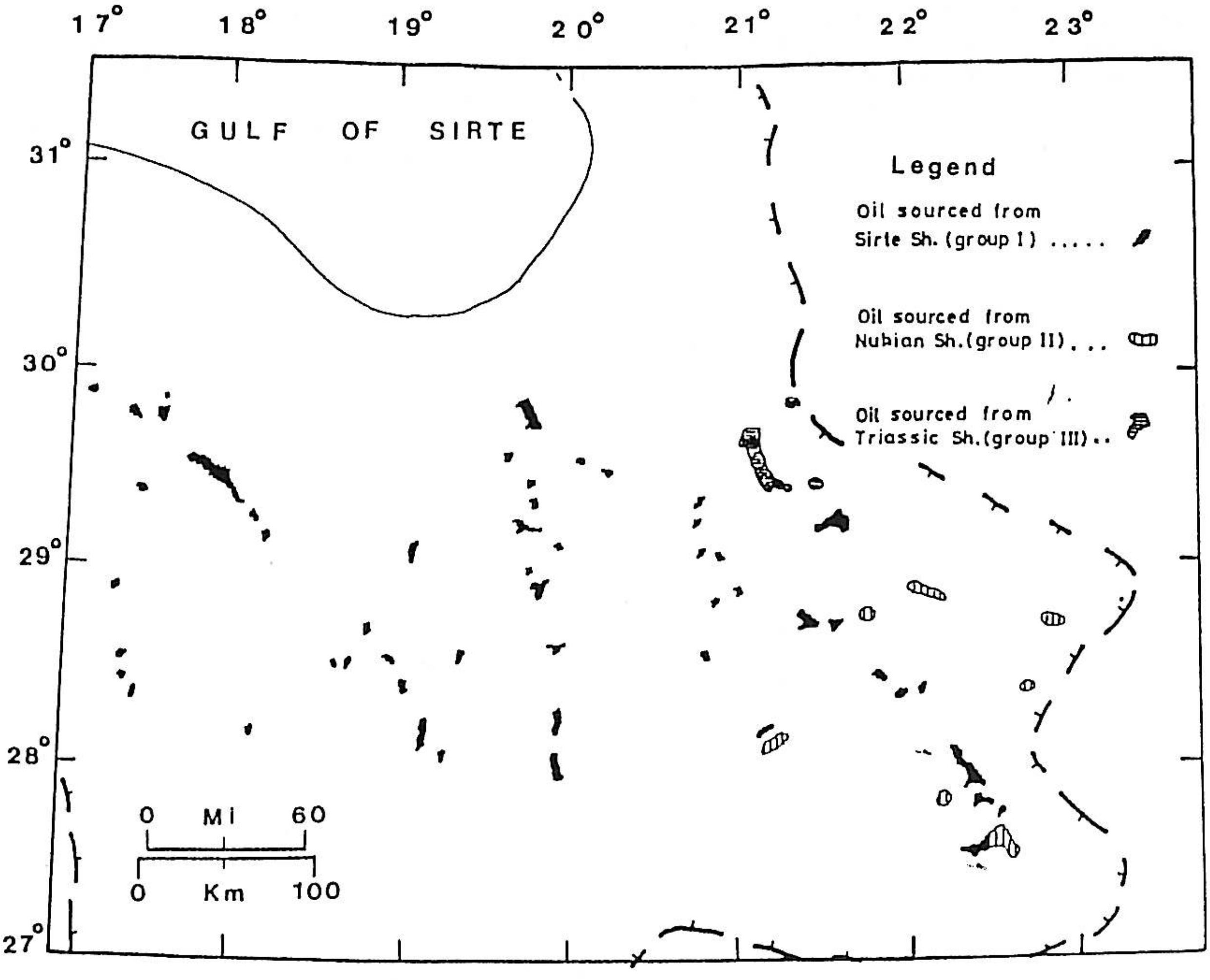

FIG. 11. Distribution of the main three groups of oil in the Basin.

GENERATION AND MIGRATION

The Sirte Shale may be considered as the source rock for the bulk of the oil of the Basin. The type rock of reservoirs varies in lithology from carbonates and sandstone to fractured quartzite and granite dating from Early Cambrian to Oligocene times.

Based on the TTI values from Lopatin's method of analysis attempted on the oil samples of well DD2a-59 (Figure 12), the time of oil generation could be estimated. The well is located in the south central part of the Agedabia Trough. The results indicate oil generation in the Early Miocene. This points out to oil-bearing potential of the Pre-Miocene traps. It is also likely that the Sirte Shale oil source rock may have entered major oil generation stage at a depth below 10 000 feet.

The structural framework of the Sirte Basin consisting of horst-graben system appears to have had a dominant role in controlling the migration routes before entrapment. The migration distances are typically short due to the tectonic style. Vertical faults across porous and permeable beds may have influenced the oil migration paths in the Basin. The migration pattern can be modeled using the present day map of the pre-Upper Cretaceous unconformity. Figure 13 depicts the relation between the Sirte Shale source rock and the possible migration paths to the trap rocks. It is evident that a majority of large oil fields occur on horst blocks adjacent to the generative depressions. A few others appear within the generative depression also.

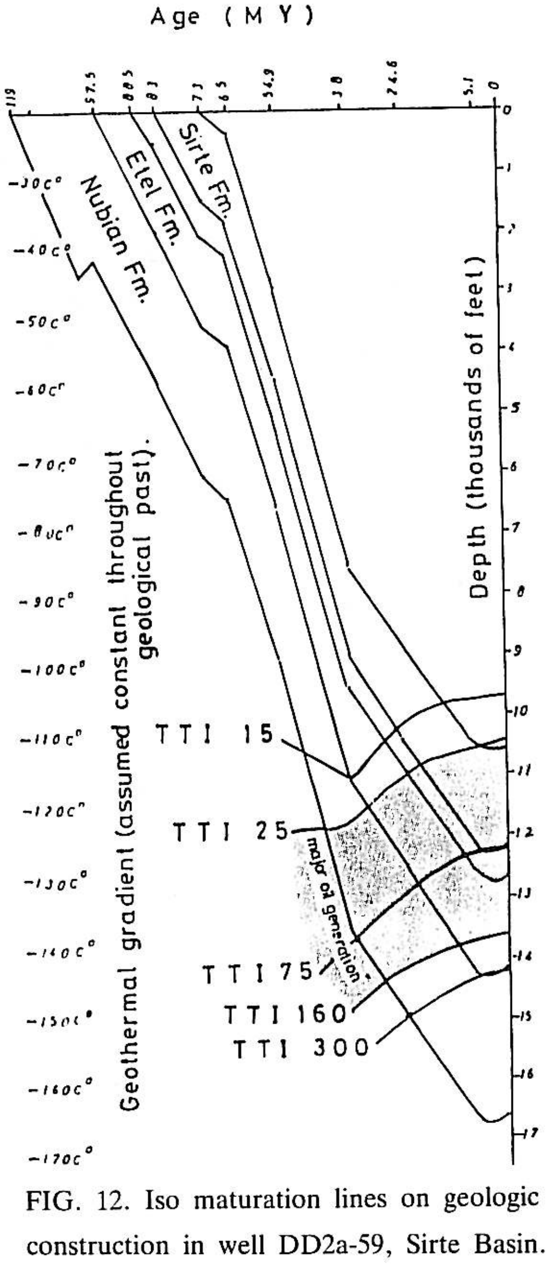

FIG. 12. Iso maturation lines on geologic construction in well DD2a-59, Sirte Basin.

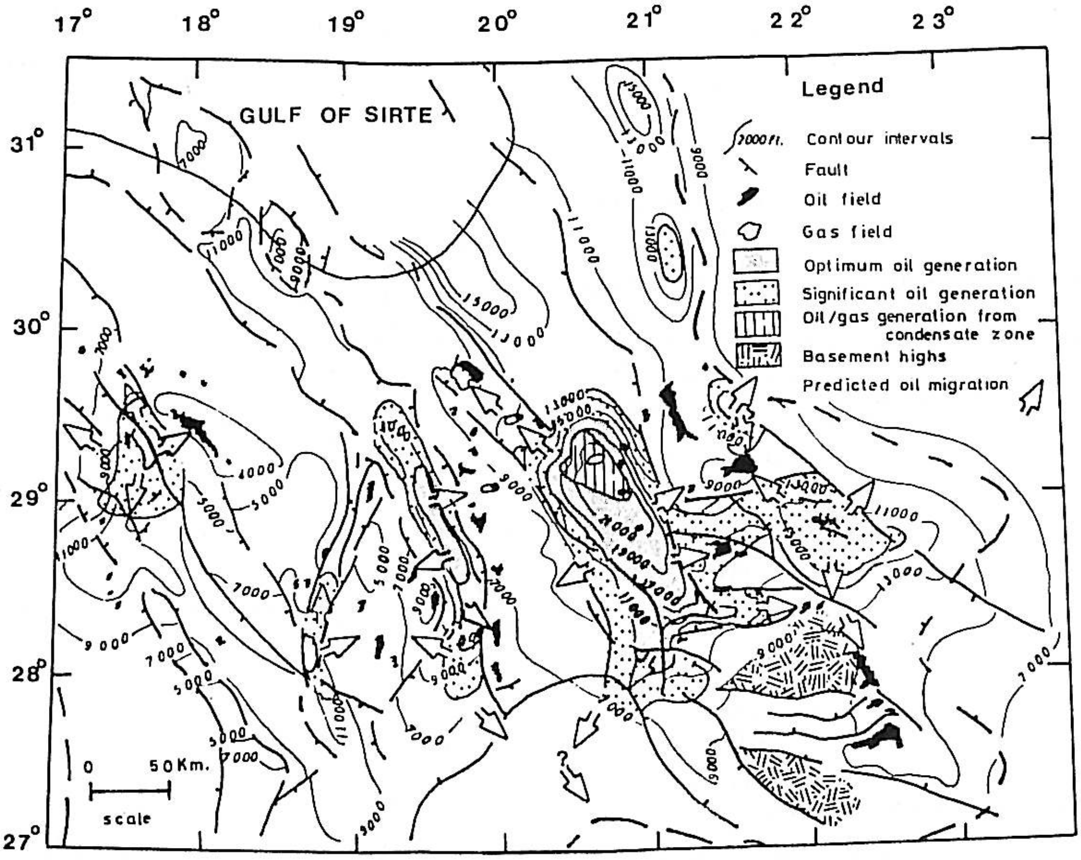

FIG. 13. The postulated migration paths of the oils generated from Sirte Shale.

The available data enables to expect additional effective source rock systems to be present in the sedimentary formations below the Sirte Shale. These may be contributing, at least , part of the oil in the southeastern part of the Basin (as for example in the Attifel Oil field) which are characterised by relatively heavier carbon isotope and excessive wax content. However, the exact positioning of the source rocks for such oils stands difficult. Generally, the lagoonal/lacustrine environment of algal-dominated source rock may have generated oils rich in the wax content. On the basis of environmental factors it may be mentioned that deposition of the source rock facies may have been fairly frequent during the Turonian and Lower Cretaceous times.

CONCLUSIONS

On the basis of geochemical data and in the light of known geologic history of the Sirte Basin, attempt has been made to provide a stisfactory explanation of source bed genesis, hydrocarbon accumulation and entrapment. The study shows that :

1. Of the Mesozoic- Tertiary sequence, the Sirte Shale (mainly of Campanian age) appears to be the most favourable source rock in containing rich and mature organic facies over a considerable part of the Basin.

2. The Sirte Shale deposited in marine reducing environment abounded in semi-silled grabens during a period of transgression. Its organic facies appear to improve gradually from type IV, III, II-III and II towards the central part of the graben system.

3. The areas of major oil generation could be mapped on a Basin-wide scale. The reservoir rocks close in and on platforms bordering the source-rock accumulations. They are deemed highly prospective areas for hydrocarbon exploration. However, the risk factor increases with distance away from the source pods.

4. The only area with late mature Sirte Shale source rock occurs in the depocenters of the Agedabia Trough (around well AA1-6). It could be a source for the gas accumulations here.

5. The oil generation from Sirte Shale source bed commenced from the Early Miocene and continued till the present time. Against this background it is likely that all traps in the Basin could be hydrocarbon bearing.

6. The tectonic style of the Basin, migration paths and oil-to source rock correlation indicate that the migration distance could be short or moderate.

7. The bulk oil has similarities with the Sirte Shale kerogen. Additional waxy crude contributes a part of the oil in the southeastern part of the Basin such as for example in the Attifel giant oil field. This crude is different from the bulk crudes in terms of all parameters examined in the present work. These waxy oils may have been derived from an algal source perhaps deposited in a lagoonal/lacustrine environment. They may belong to Middle or Lower Cretaceous Sedimentary sequences. Further studies are required to resolve the issue.

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PRJ Vol 1, (January 1989); P. 29–33, 3 TABLES.

THE ACTION OF SILVER BENZOATE AND BROMINE ON AROMATIC COMPOUNDS AND ALKANES

S . Tumi *

تأثير بنزويتات الفضة والبروم على الهيدروكربونات العطرية والالكينية

د . الصديق عمر التومى

تعرض هذه الدراسة طريق تفاعل بنزيوتات الفضة والبروم فى وسط غير متجانس من الهيدروكربونات . ومن نواتج التفاعل ونسبة الاستيرات والبرومينات وشدتها فى التفاعل مع الهيدروجينات الأحادية والثنائية والثلاثية تم التوصل الى تحديد طريقة التفاعل والتى وجد بأنها رادكل موجبة تكونت فى وسط من $(PhCO_2)_2AgBr$ و $PhCO_2Br$

ABSTRACT

Silver benzoate and bromine were used to react in heterogenous phase with certain aromatic compounds and alkanes. From the data on the ratios of bromination and bencoyloxylation products and the extent of reaction on primary, secondary and tertiary hydrogens, a mechanism has been suggested in which an electrophilic radical attack is considered most probable in the presence of $(PhCO_2)_2AgBr$ and $PhCO_2$ as intermediates.

INTRODUCTION

Several accounts of substitution reactions of aromatic compounds brought about by silver benzoate and halogens have appeared in the literature. Three different types of substitution in the ring have been observed, namely phenylation, benzoyloxy lution and helogentian. Birchenbach and Meisenheimer(1) obtained aryl benzoates and iodides from reactions of silver benzoate and iodine with anisol and with chlorobenzene at 135°C. Chlorobenzene gave a moderate yield (30%) of ortho and para-chloro-phenyl benzoates together with a little chlorobenzene.

Anisole yielded only iodoanisole in 60% yield. No evidence as to the nature of this reaction was provided.

Bryce-Smith and Clark(2) re-examined this reaction and reported the production of a solid reactive species, insoluble in most solvents with the empirical formula $(C_6H_5CO_2)_2AgI$ which appeared to cause these substitution reactions with aromatic compounds such as benzene, anisole, t-butylbenzene, chlorobenzene and nitrobenzene. The evidence for this complex was based on the analytical results from the hydrolysis of the solid.

$$3AgI(OCOC_6H_5)_2 + 3H_2O \rightarrow 6C_6H_5CO_2H + 2gI + AgIO_3$$

The analytical results support this formula for the iodide, but they are inconclusive in the case of the bromide. Similar types of complexes were suggested by Simonini(3) by Simond(4) and by Prevost(5).

Benzoly hypobromite have been postulated by previous workers as a reactive intermediate in reactions of silver benzoate and bromine but never isolated or fully characterized. The evidence for its existence was based on their addition reaction to alkanes.(6)

In this study, an attempt has been made to investigate this reaction futher and to study its mechanism as well as its synthetic potential. Five different aromatic compounds (Benzene, toluene, nitrobenzene, benzonitrile and pyridine) were chosen as substrates because of their distinct orientational behaviour towards both electrophilic and radical attack.

Alkanes are likely to be subject to hydrogen abstraction by reactive radicals and so are not unlikely to yield alkyl benzoates. Therefore, alkanes, heptane, 2 methyl butane, cyclohexane were chosen as substrates because these compounds provided examples of primary, secondary and tertiary hydrogens with an expected pattern of radical reactivity.

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Table 1. Products of Reaction of Silver Benzoate and Bromine with aromatic and aliphatic compounds

Substrate Reaction Temperature	Benzene 25°C 8 hrs Reaction Time		Toluene 20°C 6 hrs		Nitrobenzene 25°C 5 hrs		Benzonitrile 25°C 5 hrs		Pyidine 25°C over 12 hrs		2-methylbutane 25°C 8 hrs		n-heptane 25°C 6 hrs		cyclohexane 25°C 6 hrs		methyl-cyclo-hexane 25°C 6 hrs	
Strarting materials	mole	mole%	mole	mole%	mole	mole%	mole	mole%	mole	mole%	mole	mole%	mole	mole%	mole	mole%	mole	mole%
Bromine	0.0265	-	0.0184	-	0.017742	-	0.01319	-	0.03353	-	0.01255	-	0.0590	-	0.0330	-	0.05413	-
Silver Benzoate	0.0530	-	0.03579	-	0.0355	-	0.03665	-	0.0670	-	0.0062	-	0.0295	-	0.0164	-	0.05418	-
Organic products																		
Aryl & Alkyl bromides	0.0086	16.6	0.00583	16.3	0.0	0.0	0.0	0.0	0.0	0.0	0.00069	5.4	0.0025	4.6	0.002	6.3	0.005	8.4
Aryl & Alkyl Benzoate	0.00533	10..	0.00163	4.2	0.0028	8.	0.0093	25	0.003	4.5	.00072	-	0.002	4.2	0.0013	3.5	0.0023	7.5
Benzoic Acid	0.03169	59.6	0.0206	53..	0.0246	69	0.025	68	0.0368	55	0.00603	49.0	0.0025	42.5	0.028	87.3	0.029	49.0
Silver Benzoate	not calculated		0.0132	39..	0.005	1.4	0.005	0.0	0.0	0.0	0.0054	24.0	0.02	33.0	not		not calculated	

EXPERIMENTS AND RESULTS

Substitution reactions of some aromatic and aliphatic hydrocarbons

Bromine was added dropwise to a well stirred suspension of two equivalent moles of dry silver benzoate in excess substrate (benzene, toluene, introbenzene, benzonitrile, pyridine, 2-methyl butane, hexane, methyl hexane and heptane) at OC° in the dark.

The mixture was allowed to reach room temperature and maintained in that condition until the reaction was completed. The silver benzoate and silver bromide were removed by filtration. Free benzoic acid was extracted from the reaction mixture with saturated sodium hydrogen carbonate.

Unreacted substrate was removed from the organic phase by rotary evaporation. The neutral residue from the evaporation of solvent was examined by g.l.c., t.l.c. mass spect., I.R. and N.M.R where appropriate.

The products from this reaction were compared with the authentic samples and the results obtained are summarized in tables 1, 2, and 3.

DISCUSSION

Owing to the insolubility of silver benzoate in both aromatic and saturated hydrocarbons the reaction occurs under heterogeneous conditions and as can be seen from tables 1 and 2 two types of substitution may result, benzoates and bromides.

The benzoate products formed from nitrobenzene and from benzonitrile were found to be exclusively the meta isomers. These observations are compatible with electrophilic but not with typical radical displacement. Benzoyloxylation of toluene by contrast occured mainly in the side chain (97%) forming benzyl benzoate which might at first sight be considered typical of radical abstraction. The small proportion of ring benzoyloxylation that did ocur was of low selectivity (1.5% orto 0.89% meta, and 0.65% para) and of pattern similar to that of radical substitution of toluene. The benzyl benzoate obtained could arise from recombination of benzoate and benzyl radicals.

$$PhCH_2 + PhCO_2 \rightarrow PhCH_2O_2CPh$$

Table 2. Orientational preference for bromination and benzoyloxylation of aromatic compounds

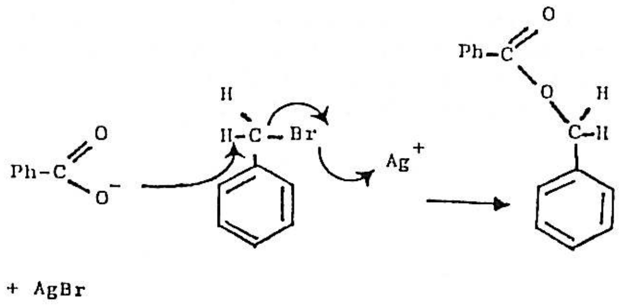
	Bromination				Benzoyloxylation			
SUBSTRATE	O-%	m-%	p-%	O attack	O-%	m-%	p-%	O attack
Toluene	30%	-	70-%	-	1.5%	0.85%	0.65%	97%
Nitrobenzene	-	-	-	-	-	100%	-	-
Benzonitrile	-	-	-	-	-	100%	-	-
Pyridine	Only 3-bromopyridine detected				Only 3-pyridyl benzoate			

Table 3. The relative amounts of primary, secondary and tertiary attack of alkanes with silver benzoate

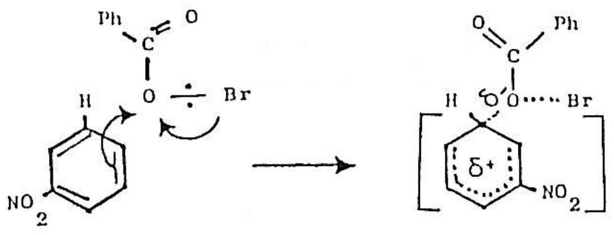
SUBSTITUTION	SUBTRATE	TERTIARY ATTACK	SECONDARY ATTACK	PRIMARY ATTACK
Benzoates	2-methylbutane	13.6	1	traces
	methlylcyclohexane	13.7	1	"
Bromides	2-methylbutane	10.4	1	"
	methylcyclohexane	28.2	1	"

This may be considered improbable because, in the present case, each reaction is at a very low concentration and phenylation products are absent.

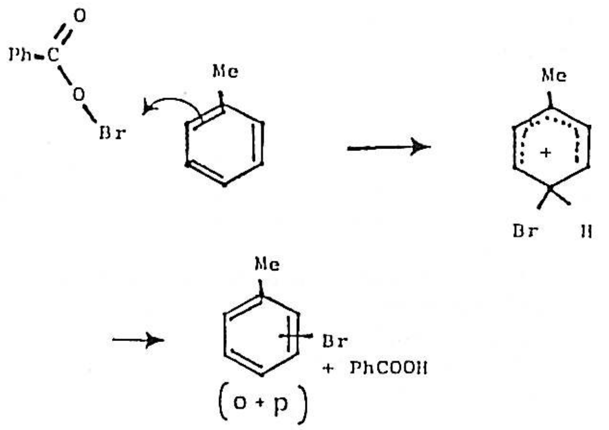
A second possible route to benzoyl benzoate could be by SN ^{2} process. In a control experiment we found that indeed, benzoyl benzoate was obtained in good yield from the reaction of silver benzoate with benzyl bromide.

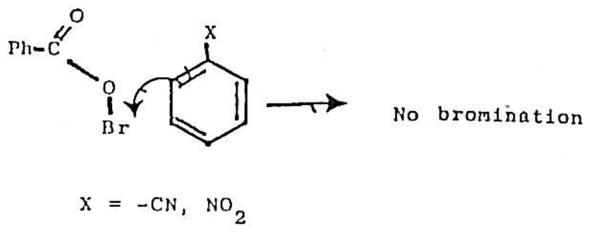


However, the unusual feature of these reactions is the oriention al preference of attack. In each case the isomer distribution remains clearly that which is normally associated with electrophilic attack. It may be inferred from these results that the radical has electrophilic character or that the transition state partakes of a degree of charge polorisation.



Nitrobenzene and benzonitrile, known to be strongly deactivated towards electrophilic attack, give no products of bromination when treated with silver benzoate and bromine while toluene yielded 16% of mixed bromotoluenes of which the ortho/para ratio was 0.43. No meta bromotaluenes were observed. This product distribution is compatible with electrophilic substitution. Furthermore the partial rate factors for bromination of toluene in this study are similar to electrophilic substitution reaction.(7)





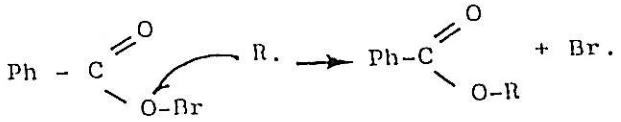
The total rate factors for benzoyloxylation are much smaller. K toluene/K benzen is 7.0. It appears that the brominating agent is highly selective while the benzoyloxylating species is of low selectivity arguing in favour of electrophilic and radical attack respectively.

In this work the benzoate and bromide products formed from alkanes which contained tertiary, secondary and primary hydrogens such as 2-methyl boutane and methyl cyclohexane amounted to 5.4-8.4%. The ratio selectivity was heavily in favour of attack at tertiary position (95%) with only little secondary (5%) and traces of primary attack. Benzoyloxylation of the secondary positions of heptane (4.5%) yield was not random, but gave as the major product 2-heptyl benzoate (65%) together with the 3 and 4-isomers (35%).

There are no available data from the literature concerning benzoyloxylation of alkanes but the product distribution is very similar to that obtained for other radical substitution reactions such as phenylation or bromination. A further possibility, however, remains to be considered. The alkyl benzoates could in principle result from a nucleophilic displacement between alkyl bromides formed by radical bromination and silver benzoate probably by a silver ion catalysed SN^2 process. In a control experiment we have investigated this possibility but found that under the reaction conditions not much displacement occurs between cylohexyle bromide and silver benzoate, in contrast to the results obtained with bromotoluene.

These results suggest that benzoyloxylation and bromination of both aromatic compounds and alkanes by silver benzoate and bromine has the general character of a radical reaction though, again, a benzayloxy radical transfer from some covalent species must be inferred. The following scheme is consistent with the facts :

$$RH + Br\cdot \longrightarrow HBr + R\cdot$$



The attack of an alkyle or aryl radical on the silver benzoate was considered unlikely since it would result in the deposition of metallic silver which was not formed.

The production of 2-bromobenzoyloxyalkane from the addition of cyclohexene or ethylene to the clear yellow solution from reaction of silver benzoate and bromine in carbon tetrachloride, suggests the presence of benzoyl hypobromite in the mixture which is either formed as such by an ionic reaction between bromine and silver benzoate or is present in equilibrium with solid in suspension, the so called "Silver bromide dibenzoate".

Therefore, we conclude that the reaction mixture consists of two components, one being the Solid intermediate $(PhCO_2)_2AgBr$ and the other appears to be a solution of benzoyl hypobromide $PhCO_2Br$.

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PRJ Vol 1, (January 1989); P. 34–36, 5 FIGS.

Short Note

FAILURE ANALYSIS OF A WIRE - LINE DUE TO CORROSION FATIGUE

A . Mazur * and F . El Shawish *

تحليل انهيار كبل معدني نتيجة كلال التآكل الكيميائي

د . آدم مازور و فوزى الشاوش

تتأثر الاسلاك المعدنية المصنوعة من الفولاذ بعملية كلال التآكل الكيميائى الذى يسبب فى قصر مدة استعمالها . ومن خلال عملية تحليل الأنهيار ، المعتمد على اساس ميكانيكية الكسر ، لكبل معدنى مقطوع لم تعمر فترة استعماله طويلا فى أحد الحقول النفطية التابعة لشركة آجيب ، تم التوصل الى توضيح ميكانيكية بدأ وانتشار التصدع خلال استعمال الأسلاك .

INTRODUCTION

Often steel wire-lines are operating in severe conditions due to alternating stresses, high bending moment and hostile environment. Therefore, the reliability of wire-lines plays an important role in securing efficiency of their multi-purpose operations.

CASE HISTORY

Few samples of 2.34 mm diameter steel wires were taken from a broken wire-line operated at a well of Agip Co. during a relatively very short time. Wire surface was smooth without the signs of general corrosion damage. The fractured surface from point A (Fig. 1) is inclined to the wire surface of about 30°.

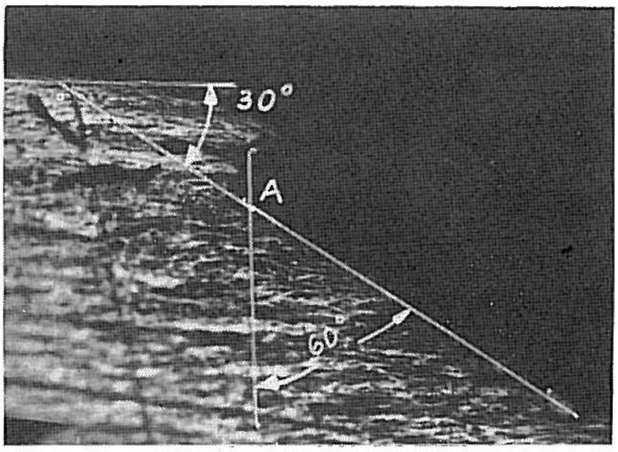

FIG. 1. Longitudinal cross-section of the broken wire-line Nital etched, magnification 300X.

The estimated maximum pull load applied during operations was 1580N. This load should not break the wire-line over a short time of operation.

RESULTS

To check the wire-line quality the two specimens were cut from the non working part. The mechanical tests were performed according to APJ Standard. 9/A Section. The results confirmed an excellent workmanship of steel-wire. It was produced from improved uncoated plow-steel of average tensile strength 1450 MPa. The reduction in area was 59%. This means that the steel-wire had enough high plasticity before the final fracture. Fractured surface of tensile tested specimens exhibited a typical ductile character.

The longitudinal cross-sections were prepared from the wire-line that failed during operation. Fig. 2 shows four short transverse cracks (marked A,B,C and D). Generally, the cracks started at a tiny surface defect similar to the corrosion pit shown by the arrow in Fig.3. After some distance (marked by A-B) the main crack changed direction along the path inclined of about 60°. Along this inclined path the crack produced a zig-zag pattern. A high optical magnification revealed that the zig-zag crack consists of short transversal (T) and parallel sections (A-A) visible in Fig. 4. Usually the transversal parts (T) ended by producing two arms (A-A).

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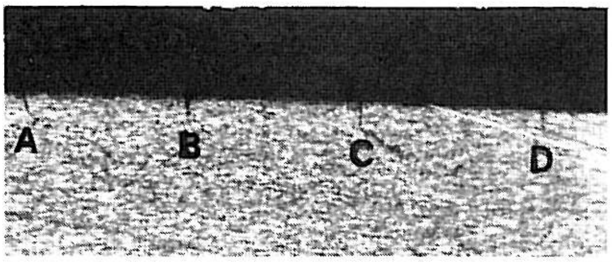

FIG. 2. Surface cracks marked by A, B, C, and D Longitudinal cross-section. Nital etched, magnification 60X.

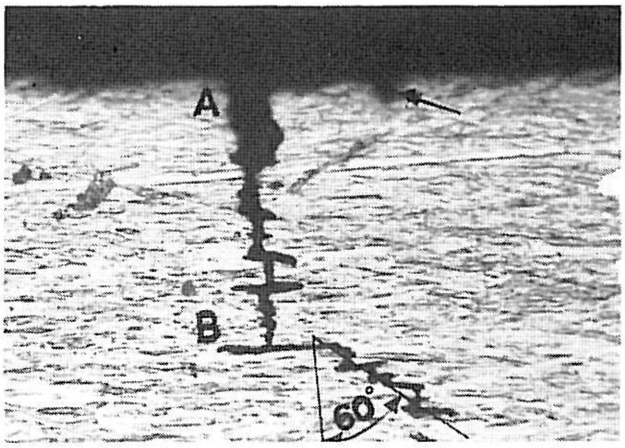

FIG. 3. Main corrosion fatigue crack started at point A. The zig-zag crack path started at point B. An arrow shows small corrosion pit as a site of corrosion fatigue crack initiation. Nital-etched, magnification 600X.

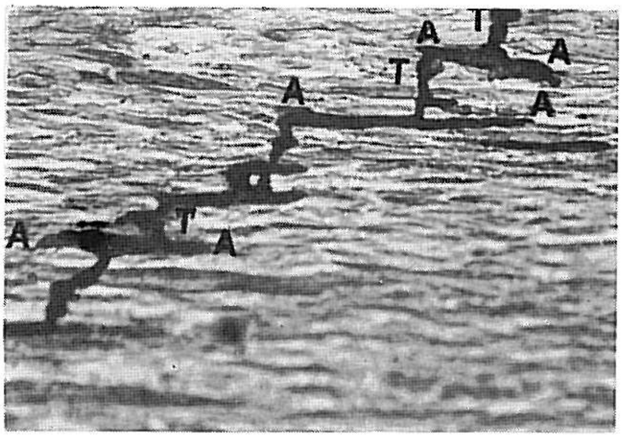

FIG. 4. Zig-zag crack pattern. Transversal part (T), parallel part (A-A). Nital etched, magnification 1200X.

DISCUSSION

A high cold drawn steel wire is characterized by unidirectional fibrous-like structure. A very high stage of cold deformation developed not only sharp crystallographic texture but also the pearlitic colonies oriented along the wire axis (1). Therefore, any of the transversal (mechanical) crack initiated at the surface had tendency to be arrested at the "interfibrous" surfaces situated parallel to the wire surface . The craks in the failed wire initiated at the tips of the small surface pits where stress concentration was high enough. Relatively low operational load produced stress which had been amplified at the wire surface by bending momentums during the passage of the wire-line over pulleys, blocks and reels. Such alternating stresses combined with the action of environment containing detrimental species like H_2S produced conditions for transgranular low-cycle corrosion fatigue cracks. Low-cycle corrosion fatigue is more destructive, for the steel, than high-frequency (2). The transversal part of the crack (section A-B in Fig. 3) was controlled mostly by bending fatigue stresses. They were high enough for crack propagation through the fibrous structure.

The corrosion also played some role in widening (dissolution effect) the upper part of a transversal crack as is cleary visible in Fig. 3. Therefore the parallel situated fibres could not effectively arrest a main crack.

According to fracture mechanics principles (3), in the situation shown schematically in Fig. 5, if the crack is longer (a / b ratio smaller) the stress-intensity factor K_I increases due to change in geometrical functions $F_{1-3}(a/b)$ as indicated by the following equation :

$$K_1 = G_N \, a \, F_{1-3}(a/b)$$

Where :

$G_N = (4M) / a^3$

G_N is the nominal stress

M is the bending momentum

physically, K_I represents the plastic zone at the crack tip(A).

If the value of K_I is higher the plastic zone is more developed and materials resistance against brittle fracture also increases . Therefore at some distance the main crack becomes effectively arrested (See Fig.3 point B) developing two perpendicular arms until fatigue-corrosion process reaches a weak structural point where the next transversal crack can break a few metallic fibers. Then again, the crack is arrested and the process is repeated (see sequences T-A, T-A etc in Fig.4). Such zig-zag crack propaga-

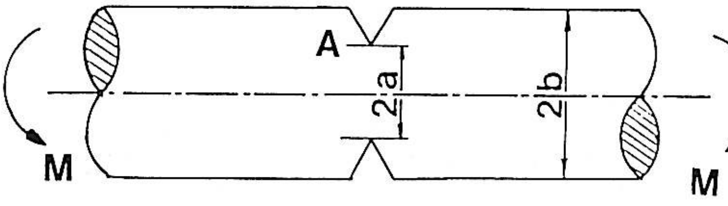

FIG. 5. Bending momentum acting in the wire with two surface cracks.

tion is typical for fracture of composite materials also. It is worth stressing that when the main crack changes the direction (about 60° inclination, see Fig.3) the process is similar to stress-corrosion cracking. It has been interpreted (4) that the stress distribution around the tip of a static crack is such that the maximum normal stress along the crack plane is significantly less than along planes inclined 60° to the crack tip. This was said to encourage development of "advance" cracks away from the plane of the main crack. Therefore, the final fracture is inclined about 60° to the transversal main crack initiated at the wire surface. Such final situation is shown in Fig.1.

CONCLUSION

Relatively short service-life of a tested wire-line was affected by low-frequency corrosion fatigue process. The wire-line operated at relatively high bending alternating stresses developed in the surface layers of the wire. The fatigue cracks have been initiated at the small corrosion pits and propagated due to destructive action of low-frequency fatigue and detrimental environment containing most probably H_2S and also Cl^{-2} in formation water. The simplest way to increase the wire-line service life is to increase the diameters of the pulleys and reels. This will decrease bending stresses at the steel wire responsible for the propagation of corrosion-fatigue crack.

ACKNOWLEDGEMENT

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PRJ Vol 1, (January 1989); P. 37-39, 5 TABLES.

Short Note

A VISCOSITY BLENDING MODEL FOR LUBRICATING OILS

A. Alem *

نمط خلط لتحديد لزوجة زيوت التشحيم

د . عبد العاطى العالم

تستعمل زيوت التشحيم فى الحياة العملية لاغراض متعددة ، وبالتالى فان مواصفاتها تختلف باختلاف تلك الاغراض ، واختيار الخلطة المناسبة من قطفات نواتج تكرير خام معين لتحضير زيت الاساس الذى هو العنصر الرئيسى للمنتوج النهائى يعتبر من أهم العوامل فى تحديد تلك المواصفات ..

ومن ناحية أخرى فان خاصية اللزوجة تلعب دورا أساسيا فى تحديد نوعية الزيت المنتج ، ويتم مراقبة لزوجة المواد المنتجة بالتحكم فى نسب خلط قطفات نواتج التقطير المستعملة فى تحضير زيت الأساس .

وتهدف هذه الدراسة لاستنباط نمط دقيق لتحديد نسبة خلطة قطفات خام البريقة الليبى لانتاج أنواع متعددة من زيت التشحيم وذلك قبل استعمال أى نوع من الاضافات أو استخلاص أى كمية من الشمع كما تهدف أيضا لحساب كمية الانتاج المتوقعة من تلك الانواع من الزيوت .

ويتوقع لهذه الدراسة أن تساهم فى تمكين مصافى التكرير التى تتعامل مع خام البريقة الليبى فى تحديد الكمية القصوى من كل نوع من أنواع زيوت التشحيم مع المحافظة على جودة هذه الزيوت من حيث مواصفاتها ودرجة خاصية اللزوجة بها ..

INTRODUCTION

Any suitable lubricating oil performance can be modified by controlling the amounts of different cuts and using additives so as to give lubricating oils a broad range of uses. Blending of different cuts of lubricating oil ranges of Brega crude had been investigated to obtain an optimum base oil before adding any additives.

Lubricating oils are best made from wax free crude oils. However, applications of solvent extraction and solvent dewaxing make it possible to use a wide range of crude oils in the manufacture of lubricating oils. The type and concentration of additives to lubricating oils vary depending on the applications, types of operations and the ranges of the cuts used in the blending program.

Lubricating oils are classified according to their viscosity. A useful system of Lubricating oil classification was developed by the Society of Automotive Engineers (1974) where maximum and minimum viscosities are specified at 110°F and 210°F, respectively.

The objective of the present study is to enable the users to determine the volume and ranges of the cuts to be used in order to obtain an optimum blend of lubricating oils. The blend must satisfy the requirements of viscosity which is essential for a given specific lubricating oil.

Cuts of Brega crude oil in lubricating oil ranges have been blended and the results are compared with the experimental work of this study. All possible combinations of the blended cuts were measured experimentally.

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EXPERIMENTAL WORK

According to the U.S. Bureau of Mines method of classification (IP Standards, 1972) the Brega crude oil is a paraffin-intermediate base crude. The characteristics of Brega crude oil are listed in Table 1.

Table 1. Brega crude oil characteristics

Property	Test method	Result
Sp.gr.15.7°C/15.7°C	IP 160	0.824
API	IP 146	40.1
Sulphur content wt%	IP 63	0.197
Viscosity at 100°C cst	IP 71	4.39
Pour point °C	IP 15	3.
R.V.P. at 37.6°C Kg/cm^2	IP 69	0.457
Flash point, °C		-5
Asphalthene content wt%	IP 143	0.072
Con-carbon (wt%)	IP 13	1.63
Ash content (wt%)	IP 4	0.014
Wax content (wt%)	UOP	4.235
Salt content	IP 77	0.024
H_2S(ppm)	Shell	102.
Characterization factor		12.30

ASTM distillation was performed using the ASTM 86/1P24 procedure (IP Standards, 1972). The crude was distilled using a batch fractionation unit made according to the ASTM D-2842 method. The unit consists of a 2.5 cm inside diameter column with a packed hight of 1.5 m. The fractionation efficiency corresponds to 15-17 theoretical trays as determined under a total reflux condition. The operating range is up to 400°c and the absolute pressure ranges from 2 to 760 mm Hg. In order to extend the fractionation beyond 400°C the residue was distilled according to the UOP 109-59 method (IP Standards, 1972). The TBP curve on the volume basis was extended beyond 400°C using probability charts. The TBP curve on the weight basis was extended beyond 400°C, using the specific gravity data collection from the fractions obtained from the UOP 109-59 procedure. It was possible to obtain 90-95 V.I. motor oils having low pour points from this crude. The 450-500°C cut is 4.1 volume per cent of crude after dewaxing. The 500-550°C fraction is 3.1 volume per cent of the crude after dewaxing. Characteristics of the lubricating oil distillates are presented in tables 2 and 3.

COMPUTING THE BLEND

Viscosity charts for viscosity blending have been developed by ASTM. The method consists of two steps; first viscosity-temperature lines of oil are plotted, then blended at constant viscosity by linear proportioning.

The above method is time consuming and is not accurate enough since it does not blend at a constant temperature, which is the usual approach. Viscosity of different cuts in the lubricating oil range connot be linearly blended. As a result, a function that is linearly dependent on temperature is proposed. A modified form of Wathler's equation (Hobson and Pohl, 1975) was used to express the viscosity as a function of temperature :

$$\ln \ln (v + 0.7) = m \, \mathrm{Ln} \, T + b$$

Where v is the kinematic viscosity in cst and T is the temperature in °F, m and b are constans.

The procedure to compute the blend of any number of cuts is based on treating the two adjacent cuts as two oils, one being light while the other is heavy. Two equations are to be solved for m and b. Blending will be conducted at constant viscosity. Light oil parameters are used to calculate the light oil temperature T_L that will have the same viscosity as the heavier oil for the next cut. A blend of the weight of light oil m_L with the weight of heavy oil m_H of the two cuts at the same viscosity v_H would be at a temperature Tx which can be calculated from the equation :

$$m_L \, \mathrm{Ln} \, T_L + m_H \, \mathrm{Ln} \, T_H = (m_L + m_H) \, \mathrm{Ln} \, T_x$$

Where T_H denotes the heavy oil temperature.

T_x can be calculated for both the light and heavy cuts. This will lead to two viscosities for the binary blend at T_x based on light and heavy cuts.

In these calculations the basic temperatures are taken to be 100 °F and 210 °F for each cut. The blend is extended by considering the first and second cut as the light component and the third cut as the heavy component. A computer program was used to include several combinations of seven cuts of the crude oil in lubricating oil ranges.

The cuts and some of the blended results are shown in Table 4. Results show that Brega crude oil is an excellent feed stock for different lubricating oil productions (Table 5). The derived model will enable the refinery to determine the maximum amount of lubricating oil that can be produced from this or any other given crude oil. Specifications on the viscosity ranges will be the only constraint. Futher work should be conducted to cover crude oils from other terminals in Libya.

Table 2. Characteristics of lube oil distillates before phenol extraction

	Light crude oil 360-400°C	Med. lube oil 400-450°C	Vis. lube oil 450-500°C	Heavy lube oil 500-550°C
Range on crude				
Vol.%	65.5-71.3	71.3-78	78 -83.8	83.8 -88
Wt%	61-67.2	67.2-74.5	74.5-80.8	80.8 -86
Yield on crude				
Vol.%	5.7	6.7	5.8	4.3
Wt.%	6.2	7.3	6.3	5.2
Mid vol.%	68.5	74.7	80.9	86
API	31.2	27.7	23.4	20.3
Total sulphur (Wt%)	0.4	0.441	0.46	0.48
Con. carbon (Wt%)	0.017	0.035	0.066	0.123
Wax content (Wt%)	23	23	19	17
Asphaltene content (Wt%)	0.05	0.061	0.12	0.132
Pour point °C	15	32	38	-
Characterization factor	11.5	11.5	11.8	11.7

Table 3. Characterization of lube distillates after phenol extraction at 400-450°C

	Before phenol extraction	After phenol extraction (1:1)	After phenol P/O (1:2)
Viscosity index	78.7	91.6	80.7
Kinematic viscosity			
cut at 37.8 °C	30.98	34.57	36.24
at 98.9 °C	4.84	5.3 1/4	5.33
Yield on crude	6.7	5.4	5.4
Pour point °C	32	-18	-
Characterization factor	11.5	11.4	11.45

Table 4. Viscosities of different cuts of lubricating oil at 100 and 210 °C

T, °C	V at 100 °C	V at 210 °C
Cut 1.280-300	3.42	1.31
Cut 2.300-320	4.65	1.54
Cut 3.320-340	6.2	1.85
Cut 4.340-360	8.0	2.2
Cut 5.360-380	11.2	2.63
Cut 6.380-400	11.73	2.77
Cut 7.400-450	26.43	4.4
Blend, all cuts	7.8	2.14

Table 5. Samples of blends and deviation from experimental results

Blend	Deviation from experimental results (%)	
	at 100 °F	at 210 °F
All cuts	-0.25	-.19
Cuts : 1+2+3+4+7	0.18	-.02
Cuts : 1+2+3+4+6+7	0.21	-.18
Cuts : 3+4+6+7	0.03	-0.21
Cuts : 1+7	0.36	0.28

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BIBLIOGRAPHY OF THE GEOLOGY OF SIRT BASIN AND CYRENAICA PLATFORM

Compiled by M.T. Busrewil *

فهرسة المراجع الجيولوجية بمنطقة حوض سرت ومسطح الجبل الاخضر

تجميع د. المبروك ابوسريويل

نظرا للاهتمام المتزايد الذى تشهده جيولوجية الجماهيرية من قبل المتخصصين فى علوم الارض الامر الذى نتج عنه نشر عدة أبحاث جيولوجيه مبتكره صدرت على هيئة مقالات علمية فى مجلات عالمية بحثيه مختلفه ، جعل ضرورة فهرسة هذه المراجع ووضعها فى متناول البحاث والمهتمين بجيولوجية ليبيا أمرا ضروريا ، حيث تم تجميع وتبويب مجموعة كبيرة من المراجع الجيولوجيه حسب الحروف الابجديه للمؤلفين تتناول مختلف تخصصات علوم الارض عن منطقة حوض سرت ومسطح الجبل الاخضر .

FOREWORD

The vast amount of information reported by various sources, on the geology of Sirt basin and neighbouring areas has continued to develop rapidly in recent years.

This work has been compiled primarily for the use of researchers who have always needed such information at hand during their studies, and is intended to be of more immediate value for those preparing postgraduate studies on specified topics of the geology of Sirt basin and Libya at large.

The main body of the bibliography is arranged alphabetically by author, and chronologically where more than one article is included by the same author. Articles by more than one author are included alphabetically under the name of the first author. This is followed by the year of publication, the title of the article and name of publication with volume and page range.

The basic information of this work has been gathered from periodicals, specialized publication of different official bodies and previous relevant work. Most of the entries cited in this bibliography are available in the Industrial Research centre, and the department of Earth Sciences, University of Al-Fateh, Tripoli. The majority of Italian language documents are available in the Department of Antiquities, As-Saraya al Hamra, Tripoli. Results of numerous valuable technical studies carried out over the last two decades are housed in the National Oil Corporation, (Tripoli) and other affiliated oil companies.

This work would not have been accomplished without the help and support of many individuals. Therefore, I wish to express my gratitude to Dr. A. Mouzughi, former General Manager of Petroleum Research centre, for his support during the preparation of this material. Thanks are also extended to Mr. M.M Elazezi of Petroleum Research Centre, and his staff and other individuals from the University of Al-Fateh and P.R.C Information Department, who have made this work possible.

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كلمة المحرر

نشأت فكرة اصدار مجلة علمية متخصصة تهتم بنشر الدراسات والأبحاث المبتكرة التى ترتبط بعلوم وهندسة استكشاف ، وانتاج وصناعة النفط منذ اكثر من سنتين .. وتبلورت الفكرة خلال اجتماعات عدة ضمت مدير عام مركز بحوث النفط وامناء اللجان العلمية بالمركز ، وذلك ايمانا بأهمية ايجاد وسيلة اتصال بين العلماء والمتخصصين ، وخلق وسط لأنتشار المعرفة فيما يبتكر فى هذه المجالات وما يواكب ذلك من تطور وتقدم علمى وتقنى فى عالم النفط ..

وبعون من الله وتوفيقه ، ومع مطلع السنة الجديدة 1989م نقدم العدد الأول من مجلة بحوث النفط .. انها بداية متواضعة .. وليست باليسيرة .. وكلنا أمل وثقة فى ان تجاوب وتعاون البحاث والمتخصصين والنقاد من خلال مساهماتهم ونقدهم البناء سيكون الحافز لما يبذل من مجهودات للوصول بهذه التجربة الى الأفضل .. هذا ما نصبوا اليه .. نسأل الله التوفيق ..

امين لجنة التحرير

مجلة بحوث النفط

تهدف مجلة بحوث النفط إلى نشر الأبحاث المبتكرة وغير المنشورة سابقا بجانب غيرها من الاعمال العلمية كالمذكرات المختصرة العلمية التي تقع ضمن مستهدفات المركز في المجالات التطبيقية والنظرية التي ترتبط اساسا بفروع علوم هندسة النفط والهندسة الكيميائية ، والجيولوجيا ، والجيوفيزياء ، والجيوكيمياء والكيمياء . .

وتدعو المجلة جميع المتخصصين في هذه المجالات داخل البلاد وخارجها للاسهام بجهودهم واعمالهم في سبيل تحقيق هذه الغاية السامية . . وحفاظاً على المستوى العلمي للبحوث والدراسات المقدمة تستعين لجنة التحرير بالمتخصصين وذلك للتقييم العلمي للبحوث المقدمة للنشر . .

شروط وقواعد النشر :—

1 - تقدم النصوص من أصل وثلاثة نسخ بإسم أمين لجنة التحرير باللغة العربية واللغة الإنجليزية مرحليا . .

2 - تدون الصفحة الأولى من النص المقدم بعنوان البحث والذي يجب أن يكون مختصرا قدر الإمكان ويلي العنوان المعلومات الخاصة بالمؤلف — أو المؤلفين — وتشمل الإسم وعنوان الهيئة التي ينتمي إليها . .

3 - يسبق المقدمة وعلى صفحة مستقلة للنصوص المقدمة ، عدا المذكرات المختصرة موجز باللغة العربية والانجليزية محتوى كل منها 100–200 كلمة ، الموجز يجب أن يركز على النتائج التي توصلت إليها الدراسة . .

4 - تقدم النصوص على ورق مطبوع على وجه واحد وعلى مسافات مزدوجة ، ويترك هامش كافٍ من أعلى وأسفل الورقة . .

5 - تكتب المعادلات عدا البسيط منها الممكن طباعتها بالالة الكاتبة العادية أو (WORD PROCESSOR) بالحبر الأسود . .

6 - تقدم الأشكال والجداول على صفحات مستقلة ، مرتبة ومرقمة حسب ورودها في النص مع عنوان توضيحي لكل منها ، وينبغي أن يكون رسم الأشكال بالحبر الصيني . وباستخدام ادوات التحبير والكتابة ، وذلك على ورق أبيض أو شفاف من نوع جيد ، كذلك تقبل الأشكال والجداول المرسومة بالعقل الآلي على الا يزيد قياسها عن 21 × 28 سم ، وتقدم عناوين الأشكال في صفحة منفصلة . .

7 - تطبع العناوين الرئيسية للنص بالحروف الكبيرة في وسط الصفحة أما العناوين الثانوية فتطبع بالحروف الكبيرة مبتدئة من أول السطر ويليها طباعة النص في السطر التالي . . بالنسبة للعناوين أقل درجة فتطبع بالحروف الصغيرة ويوضع تحتها خط ويتبعها علامة شرطه ويليها طباعة النص مباشرة . .

8 - تعطي في نهاية البحث قائمة بالمراجع المستخدمة ، ويكون ترتيبها حسب ابجدية اسماء مؤلفيها أو ترقيمها في النص — طبقا للقواعد المعمول بها عالميا في كل تخصص — وذلك على النحو التالي :—

مراجع المجلات :—

اسم المؤلف ، سنة النشر ، عنوان المقال ؛ اسم المجلة ، رقم المجلة ، بداية ونهاية الصفحات .

مراجع الكتب :—

اسم المؤلف ، سنة النشر ، عنوان الكتاب ، اسم الناشر .

9 - لكل مؤلف ينشر بحثه الحق في الحصول على «25» نسخة مطبوعة من البحث مجانا . .

10- تكون جميع المراسلات على العنوان التالي :—
— لجنة تحرير مجلة بحوث النفط . .
— مركز بحوث النفط ص . ب . 6431 .
— طرابلس/ج . ع . ل . ش . إ . ع . .

«المعرفة حق طبيعي لكل انسان»

تقديم

يسر مركز بحوث النفط ان يقدم العدد الأول من مجلة النفط وهي مجلة علمية متخصصة تعني بالابحاث والدراسات في مجال الصناعات النفطية والبتروكيماويات ، مساهمة من المركز في مواكبة التطور والتقدم العلمي والتقني في عالم النفط . .

يهدف مركز بحوث النفط باعتباره احد مشاريع المؤسسة الوطنية للنفط إلى إجراء ابحاث في مجالات الاستكشاف واستغلال النفط والحفر والتكرير والبتروكيماويات والتآكل ودراسات تلوث البيئة بالاضافة إلى إجراء اختبارات مراقبة الجودة للمنتجات النفطية والبتروكيماوية ووضع المواصفات القياسية لها حسب الطرق والقياسات العالمية .

وفي الوقت الذي تسجل فيه ادارة مركز بحوث النفط شكرها إلى لجنة التحرير على ما بذلوه من مجهودات لابراز هذه المجلة إلى حيز الوجود تدعو جميع البحاث والمختصين إلى المساهمة والمشاركة في تطوير هذه المجلة والله الموفق ، ، ،

«د. مصطفى عامر صوله»
مدير عام مركز بحوث النفط

مجلة بحوث النفط

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العدد الاول اى النار 1989

مجلة بحوث النفط

الهندسة

الاستكشاف

الكيمياء

مقالات مختصرة

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