The Environmental Impact Of Gaseous By- Products and Pollutants

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in Waste Water At Khartoum Refinery.

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B.Sc. Architectural Engineering -Architecture Section Faculty of Engineering Ain Shams University Cairo-A.R.E

A Thesis Submitted in partial Fulfillment for the

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2005

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Crude distillation Unit (CDU)



Residual oil catalytic cracking Unit (RFCC) . and Reforming Unit(REF)



Distillation Columns Building (DCS) (Fractionator)



Tanks of Liquid petroleum gaz. (Spherical tanks)

Frontipiece : Showing The Refinery and it's main units

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الاهداء قال تعالى فى كتابه الكريم: يسم الله الرحمن الرحيم: (ووصيدًا الإنسان بوالديم حملتِه أمه وهذا على ومن وفصاله في عامين أن أشكر لي ولوالديك إلى المصير). حدق الله العظيم" سورة لقما ن" الى امى الحبيبه: لن اجد ابلغ من كلام الله عز وجل ولا اصدق من كلام الرسول صلى الله عليه وسلم الذي جاء في الحديث الشريف (جاء رجل اللي رسول الله حلى الله عليه وسلم وقال من احق الذاس يحسن صحابتهي رقال امك, قال ،قلبتم ثم من , قال امك, قال ؛قلبتم الى ابى الحبيب: لقد عملت وكافحت وجاهدت. حتى لاح اسمك علما يرفرف في سماء السودان وربيت وغرست حتى اتت ثمارك أكلها ربنا يحفظكما لنا و يمن عليكما بنعمة الصحة والعافيه. الى ابى وامى اهديكما هذا العمل المتواضع عرفانا منى بجميلكما ارجوان تتقبلاه مني. إلى زوجي د. الفاتح محى الدين تلب: اقدم لك أسمى آيات الشكر والتقدير على دعمك المادى والمعنوى طوال مشوار حياتي وعاجزة عن الشكر. الى ابنائي الاحباء: اهديكم هذا العمل المتواضع ليكون نبر اسات لكم في هذه الحياة فعلى طريق العلم سيروا. Acknowledgements

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This humble effort would not have been possible without the help of others. I would like to thank my supervisor **Dr.Abdel-Halim Hassan El-Nadi** for his continuos and exceptional help and guidance.

I would also like to extend my thanks to the KRC engineers for acquainting me with the different activities in the various Units of the KRS and helping me with the analysis of SO_2 , NO_X and CO.I should also thank the staff of the Ministry of Energy and Mining and the Sudan Petroleum corporation for access to their reports . My thanks should be extended to the Central Petroleum Laboratories (CPL) personnel for allowing me to carry out the pH, sulphide, nitrogen and ammonia, phenols, the chemical oxygen the total suspended solids(TSS), the demand (COD), biological oxygen demand (BOD) as well as oil and grease analyses. I would also like to extend my thanks to the Akadabi Group Factories for steel buildings for their help and permission to carry out this research.

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Abstract

Sudan has become one of the oil producing countries since 2000. Petroleum as an energy source represents 16 % of the energy balance of the country. The processes of prospecting, transportation, refining and utilization of petroleum may have serious negative impacts on the environment. This study focuses on the determination of the nature and concentration of the main gases ensuing during the process of oil refining, as well as the determination of pollutants in waste water at Khartoum Refinery. Also, investigation into means and ways adopted by the Refinery to reduce the negative impact of those pollutants on the environment are reviewed. The gaseous by- products analyzed include SO2, NO_X and CO. The waste water pollutants analyzed include the pH, oil and grease, sulphides, phenols, nitrogen and ammonia, the total suspended solids (TSS), the biological oxygen demand (BOD), and the chemical oxygen demand (COD). It is found that the analytical results of the gaseous by -products are compatible with the Chinese, Global Bank Guide and The Sudanese Standards. The results of the analyses of the pollutants in the outlet waste water after treatment are compatible with the Chinese and Sudanese Standards as regards oil and grease ;phenols; nitrogen and ammonia; the total suspended solids ; the biological oxygen demand and the sulphide .This demonstrates the effectiveness of the treatment methods adopted by the Refinery in dealing with the above -mentioned gaseous by-products and water pollutants . However, the methods adopted in controlling the pH and the chemical oxygen demand needs revising.

Some recommendations are proposed in order to curb the impact of this industry on the environment. DECCERCICE IN CONCERCICE

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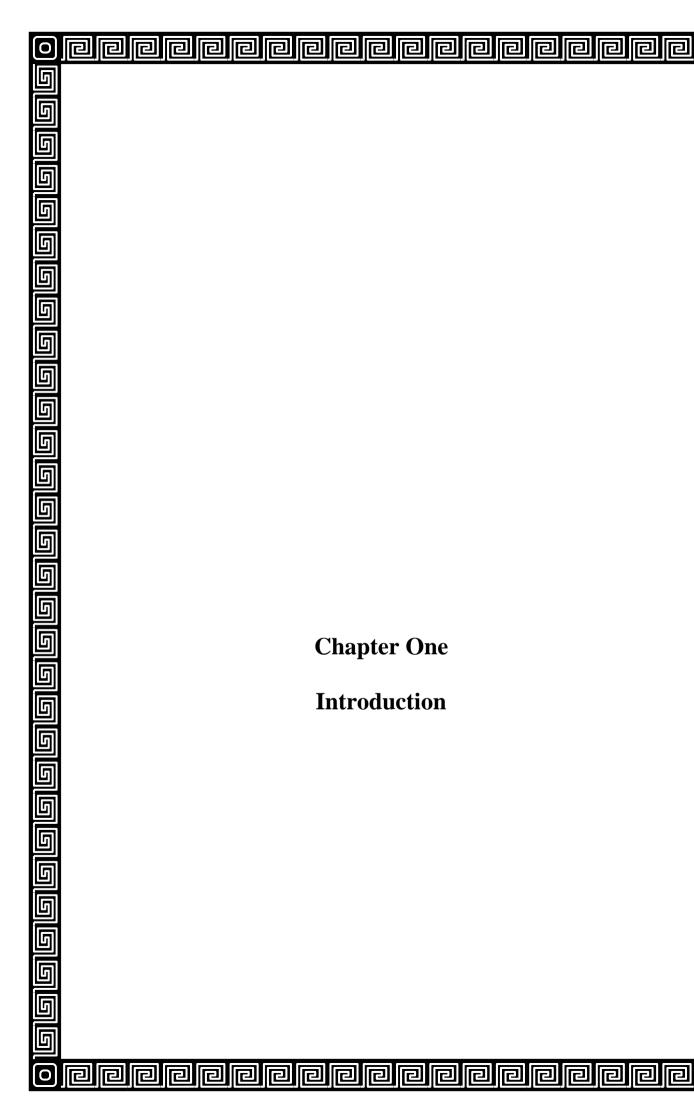
فى العام 2000م أصبح السودان في عداد الدول المنتجة للبترول, حيث يمثل فيه البترول 16 % من ميزان الطاقة. إن صناعة البترول في كل مراحلها من الإستكشاف, الإستخراج الترحيل التكرير, والتصدير وحتى الاستخدام قد يكون لها آثار ضارة على البيئة وصحة الانسان .

هذه الدراسة ركزت على تحديد طبيعة وتركيز الغازات الناتجة والمنبعثة وكذلك تحديد الملوثات في فضلات المياه الناتجة من عملية تكرير البترول بمصفاة الخرطوم هذا بالإضافة الى التعرف علىالطرق المتبعة في المصفاة لتقليل الآثار السالبة لهذه الملوثات على البيئة .

الغازات الناتجة التى حللت شملت SO₂, NO_X, CO . أما الملوثات التى حللت فى فضلات المياه بعد معالجتها شملت الرقم الهيدروجينى (pH) , الشحوم والزيوت , الكبريت ، الفينول , النيتروجين والأمونيا , المواد العالقة الصلبة الكلية (TSS) , الحاجة البايوكيميائية للأكسجين (BOD), الحاجة الكيميائية للأكسجين (COD).

كانت نتيجة التحاليل بالنسبة للغازات الناتجة أنها متلائمة مع المقاييس الصينية و السودانية و البنك الدولى للغازات الناتجة من عملية تكرير البترول كذلك نتيجة التحاليل للملوثات الموجودة فى فضلات المياه الخارجة بعد المعالجة فإنها متلائمة مع المقاييس الصينية والسودانية لفضلات الموجودة فى فضلات المياه الخارجة بعد المعالجة فإنها متلائمة مع المقاييس الصينية والسودانية لفضلات المياه الناتجة من عملية تكرير البترول بعد المعالجة فإنها متلائمة مع المقاييس الصينية والسودانية المحاليل الملوثات الموجودة فى فضلات المياه الخارجة بعد المعالجة فإنها متلائمة مع المقاييس الصينية والسودانية لفضلات المياه الناتجة من عملية تكرير البترول بعد المعالجة فإنها متلائمة مع المقاييس الصينية والسودانية لفضلات المياه الناتجة من عملية تكرير البترول البترول البترول والأمونيا والأمونيا والمواد العالقة الصلبة الكلية (TSS) والحاجة البايوكيميائية للأكسجين (BOD) والكبريت وهذا يدل على فعالية المعالجات المتبعة من قبل إدارة المصفاة البايوكيميائية الذكر من الغا زات و فضلات المياه .

أما المعالجات المتبعة للتحكم في الرقم الهيدروجيني (pH) و الحاجة الكيميائية للأكسجين (COD) فانها تحتاج الى مراجعة نسبة لعدم فعاليتها في الوصول الى التركيز المناسب. الدراسة شملت جملة من التوصيات من اجل الحد من الآثار السالبة لهذه الصناعة على البيئة.



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<u>1.1 General :</u>

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There is increasing concern among scientists and decision-`makers about the negative impact created by the use of various types of energy on the environment. Problems of desertification , global heating, climatic changes and drought surmount the deleterious impacts of these activities. Since energy is inevitable in everyday life and in agricultural and industrial activities; and that the need for it is continual, great attention is nowadays being directed towards research into the deleterious impacts of energy use on the environment. The seeking of ways and means for reducing such impacts is becoming of paramount importance.

<u>1.2 Statement of the problem:</u>

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Sudan has become one of the oil producing countries since 2000 .Petroleum as an energy source represents 16 % of the energy balance of the country .Taking into account the

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petroleum industry benefits to the economy of Sudan and the expected amelioration of life standards of its people, the processes of prospecting, exploration, transportation, refining and utilization of petroleum may have serious negative impact on the environment. This study focuses on:-

A / Knowledge of the nature and concentration of the various gases ensuing during the processes of refining at Khartoum Refinery.

B/ Knowledge of the nature and concentration of pollutants in waste water resulting from the refining process.

C/ Critical reviewing of the methods of treatment and management procedure followed by Khartoum Refinery in decreasing the pollutants to the minimum possible level.

1.3 Objectives:

1/ Determination of the various ensuing gases during petroleum refining at Khartoum Refinery, using the laboratory facilities available at the Refinery and the Central Petroleum Laboratories in Khartoum. <u>e de la constant de </u>

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2/ Determination of pollutants in the waste waters resulting from crude oil refining during the refining process, using the facilities available at the Central Petroleum Laboratories in Khartoum.

3/ Proposal of recommendations to curb any possible environmental hazards.

1.4 Location and accessibility of the study area:-

The Khartoum Refinery is located on a semi rockydesert land 15 km north-east of Al-Gaili village, and about 12 km. east of the River Nile (Fig.1 a and b). Small villages are scattered around the Refinery area whose inhabitants are mainly farmers and sheepherders, either illiterate or having incomplete primary education. However, some young men work as casual labourers in the Refinery (Khartoum Refinery Company Report, 2002).

<u>1.5 Previous work</u> :

Hassan (1981) wrote an M.Sc. thesis on the traffic and noise pollution in central Khartoum city area .The thesis focused

Deceeceece ٦ ٦ Ы on air pollutants such as carbon monoxide and sulphur dioxide and their effects on human beings .Van gils (1982) investigated the air pollution control methods and equipment in the oil refining industry. Bakhiet (1999) studied the effects of the liquid petroleum gas as an engine fuel in Khartoum State. The Ministry of Energy and Mining (2000) wrote a general report on the impact of petroleum industry on the environment .The report surveyed the ٦ P G

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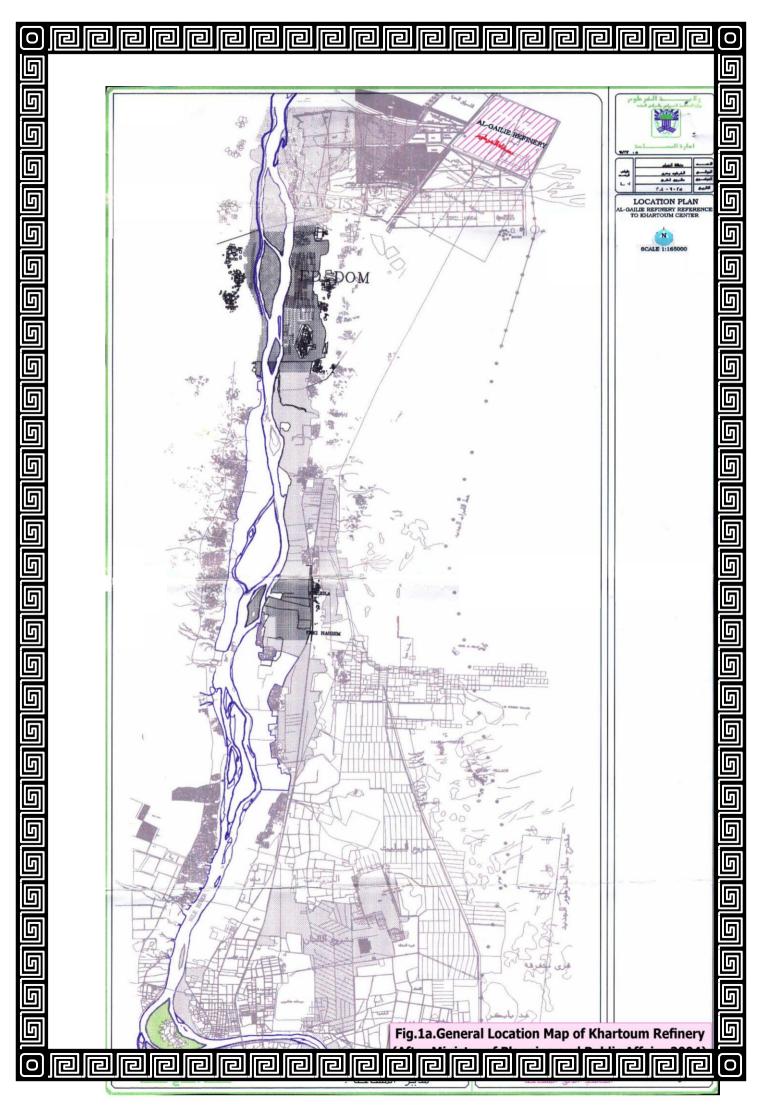
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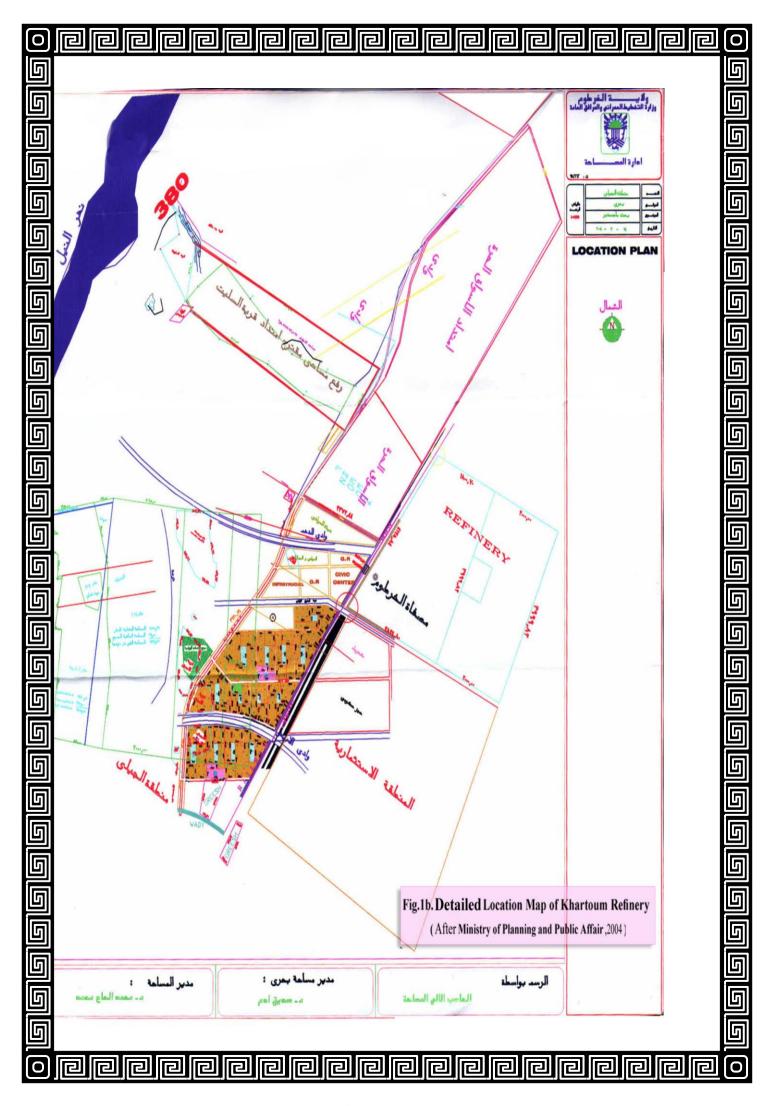
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general aspects of the impact without details or emphasis on the gaseous products of the refining process. The Khartoum Refinery Company (KRC, 2001) wrote a report on the Global Bank Guide for air quality showing the maximum standard levels of gaseous emissions of NO_X , SO_2 and CO.

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The Institute of Environmental Studies (2002) published the proceedings of the seminar on "Health Education". The seminar dealt with acid rain, green house effect and the gaseous pollutants like NO_X , SO_2 and CO. The KRC also investigated in its annual report (2002) the gaseous by- products, waste water pollutants and the KRC solid waste resulting from oil refining processes, the system management as well as the monitoring procedures applied at the Refinery . The Sudanese Petroleum Corporation, Ministry of Energy and Mining (2002) wrote a report on the regulations of the protection of the environment in the petroleum industry concerning the exploration, transportation, refining, exportation and standard limits of

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liquid wastes and gaseous emissions resulting from petroleum refining. The KRC (2003) designed the products balance flow charts .The flow chart showed the Refinery main units and their by-products. The history of the Sudanese petroleum was published in the internet together with the issue of health and clean air with emphasis on the NO_X effect on human health and (www.sudani.co.za, ecosystem htm. and www.healthandcleanair.org, 2002 and 2003).

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The Ministry of Planning and Public Affairs (2004) prepared a showing the location of Khartoum Refinery. The Petroleum Training Center (2004) published the proceedings of the course on water quality and treatment management for hydrocarbons waste water. The Sudan Engineering and Digital Information Center (2005) prepared a map showing the location of the various oil prospecting and exploration Blocks.

1.6 Materials and Methods:

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This work is concerned with the analysis of the gaseous products, and of the pollutants in the waste water resulting from crude oil refining at Khartoum Refinery. The gaseous by- products analyzed include SO₂, NO_x and CO.

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These were analyzed at the Refinery laboratories using SO_2 analyzer (for SO_2 determination), NO_X analyzer (for NO_X determination) and CO analyzer (for CO determination).

The measurements were taken during the period 20/2/2004 to 20/3/2004 when NO_X, SO₂ and CO were recorded at midday as average readings. During the field visits, the results of the analysis are read off directly from the screen attached to each device

The pollutants analysed in the waste water samples (kept in glass and plastic bottles) include the pH , sulphide , nitrogen and ammonia , phenols, the chemical oxygen demand (COD), the total suspended solids(TSS) , the biological oxygen demand (BOD) as well as oil and grease. These parameters were analysed at the Petroleum Training Center waste water lab using The pH Meter (for pH determination) , UV Spectro Photometer (for sulphide, nitrogen and ammonia, and phenol determination),TSS Water Bath (for total suspended solids Γ

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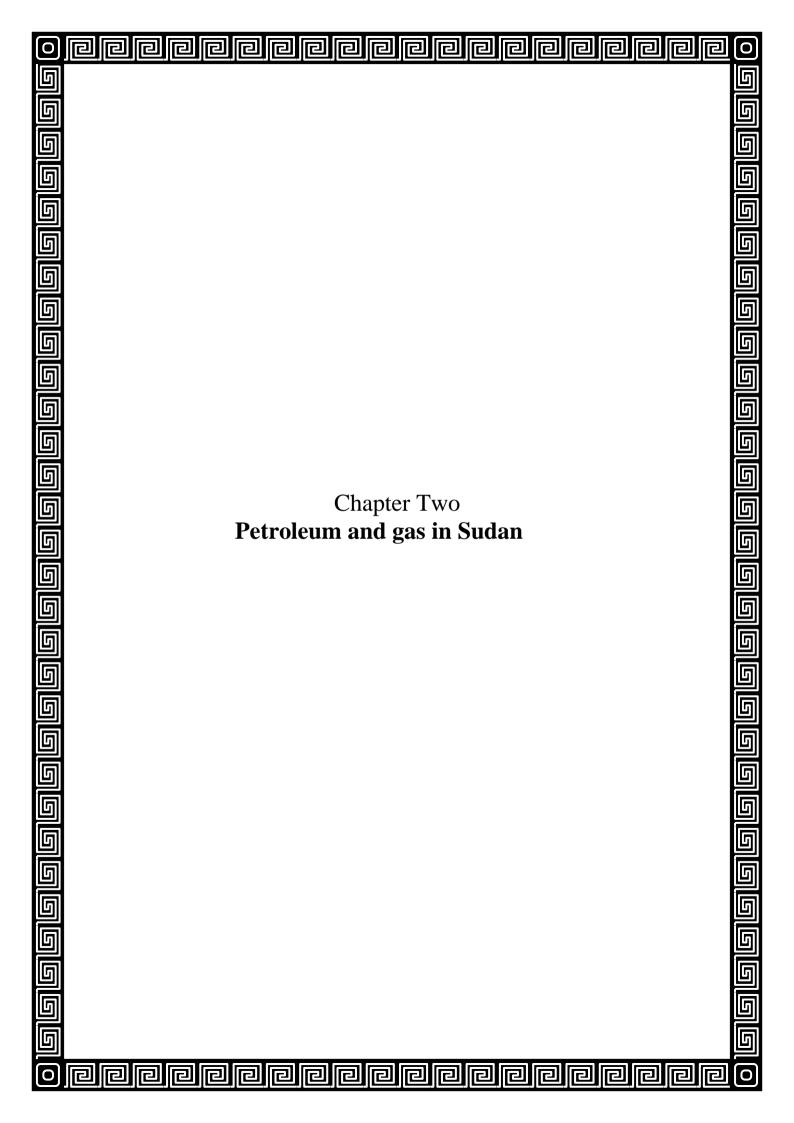
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determination), COD Reactor (for chemical oxygen demand determination), BOD Incubator (for biological oxygen demand determination), Rota Vaporate, Soxlet Extraction and Oven (for oil and grease determination).



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2.1 Introduction:

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Sudan continued to prospect for its petroleum reserves for about half a century in cooperation with some foreign companies. The great burden of the importation of petroleum materials on the Sudanese balance of payment was one of the main reasons which made the prospecting efforts reach its maximum through the last ten years. The government considered petroleum as one of the basic pillars of its economic strategy, and consequently opened the door of investment for a number of international petroleum companies.

2.2 Geologic setting :

The geology of Sudan is extremely diverse encompassing a variety of metamorphic, igneous and sedimentary rocks of various ages and tectonic settings. Fracturing and rifting in the basement rocks led to the formation of grabens that received sedimentary clastic material along with its organic contents (animal and plant remains). With increase in temperature and pressure in those basins, the organic matter decomposed to form

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The oldest sedimentary rocks encountered so far in the country are of Cambro-Ordovician age and younger, mainly from the Mesozoic era. These occur within narrow grabens in north and northwestern Sudan. Much attention was given to the rift - related basin systems in south central and central Sudan, compared with those in north central and northern Sudan. The gravity, seismic and drilling data acquired in the interior basins of Sudan indicate that more than 30000 feet of clastic sediments occur, for example, within the Muglad basins. The sediments intercalated sandstones, claystones, siltstones, include mudstones and shales .Intrusive rocks(sills) were encountered in some wells such as in Garad-1, Sobat –1 and in Tabaldi-

In the Muglad Basin , the Abu Gabra Formation which is the main source rock, consists of dark lacustrine shales containing a typically waxy kerogen. It also proved to be a reservoir rock in Block # 6. On the other hand, the Bantiu, the Darfur Group of sandstone members, the Amal and the Tendi

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Formations constitute principal reservoirs. The shales and claystones within the Abu Gabra Formation, as well as the shales and claystones within the Darfur Group form seal rocks to the underlying oil- bearing horizons.

The Sudanese interior basins are correlatable in their evolution with the west central African rift systems. They were formed during late Jurassic to early Cretaceous periods when Africa was separating from south America consequent to the opening of the south Atlantic ocean and the development of the Central Africa Shear Zone .The structural development of the largest basin (the Muglad basin) is marked with major rift cycles and sagging characterized by upward coarsening of the sequence of the clastic sediments (www.sudani.co.za, htm, 2002).

2-3 History of oil exploration in Sudan:

2.3.1 The Red Sea area:

Hydrocarbon exploration activities in Sudan date back to the years 1959-1964, when the Italian Agip Company was granted the first exploration permit in the Red Sea area. The Italian company drilled 6 wells, two of which proved the presence of

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hydrocarbons. Later , three wells were drilled by Chevron Company (1975-1977), one at Bashair which contains natural gas .The second well was drilled at Suakin archipelago 40 km off the coast of Red Sea, which contains natural gas and condensate .The third well was located south of Suakin, but was found to be dry. During the years 1989-1999 the Sudanese government signed and concluded a number of agreements with various petroleum companies including the two Canadian companies IPC and SPC in 1991 and 1993 (Ibrahim, 1982).

2.3.2 Central and Southern Sudan:

In 1974, Chevron Company signed an exploration and production sharing agreement (EPSA) with the Sudan government to explore for oil and gas in a concession area of 516000 sq. km. in central and south central Sudan. After conducting extensive geological and geophysical work, Chevron started drilling operations, which led to the first oil discovery of Abu Gabra in 1979. In 1980, Chevron discovered the Unity oil field, followed by Heglig, Talih, Sharif, Adar - Yale oil fields (Ibrahim,op.cit) .

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Total Oil Company signed an EPSA in 1980 with the government for oil prospecting in Block (B). The company conducted geological and geophysical work and defined prospects for exploration drilling. Due to the breakout of war in southern Sudan, the Total Company suspended its drilling operations. Later in 1982, Sun Oil Company was awarded a concession in central and northern Sudan. The company drilled six wells .However, no significant hydrocarbon discoveries were encountered and consequently the Oil Company terminated its contract in 1990. In August 1993, the State Petroleum Company (subsidiary of Arakis) signed an EPSA with the Government in Blocks 1,2 and 4 (Fig.2). The Company discovered very significant oil accumulations in Toma South, El Tor, El Nar and Um Sudd oil fields. In August 17, 1995, the Government and the Gulf Petroleum Company signed an EPSA for the development of Adar -Yale oil fields (Block 3d). In September 1995, the government and the China National Petroleum Corporation signed an EPSA to be executed in Block (6, Fig.2) .The company drilled successful appraisal wells based on 3D seismic Ο

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work ,two of them in Abu Gabra field and the third in Shariaf field . In march 1996 a consortium group, which includes CNPC, PETRONAS, SUDAPET and STATE PETROLEUM COMPANY (SPC) signed agreements for conducting upstream and downstream operations in Blocks 1, 2 and 4, originally acquired by (SPC). In October 1998, Talisman took the share of the State Petroleum Company in the consortium. In March, a consortium composed of the Gulf Petroleum Company Ltd. and the SUDAPET Ltd. signed an EPSA in Blocks 3d,3f and 7E.

The result of geological and geophysical surveys in the different parts of the country is the drilling of 95 exploration wells, 46 of which were productive. Examples are the fields of Sawakin, Abu Jabra , Sharif ,the Unity , TaIih , Hejlig, Adar –Yale and Kaikang.;the Gulf Company in 1995;the Chinese National Petroleum Company (CNPC) in 1995 and the Consortium Company in February 1997. The International Company GNPOC was established in 1997 .As a result a number of the exploration companies carried their work in the different parts of the country (www.sudani.co.za, htm, 2002).

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The joint venture agreement of the Khartoum Refinery Company (KRC) was signed in March, 1997 between CNPC and the Ministry of Energy and Mining (MEM) of Sudan. After that an expansion agreement of the Refinery has been signed between the MEM and CNPC in July 2003, as an addendum to the KRC construction agreement. The extension construction agreement between the KRC and CPECC has been signed in April, 2004. (Al Ray Alaam Daily , 2005).

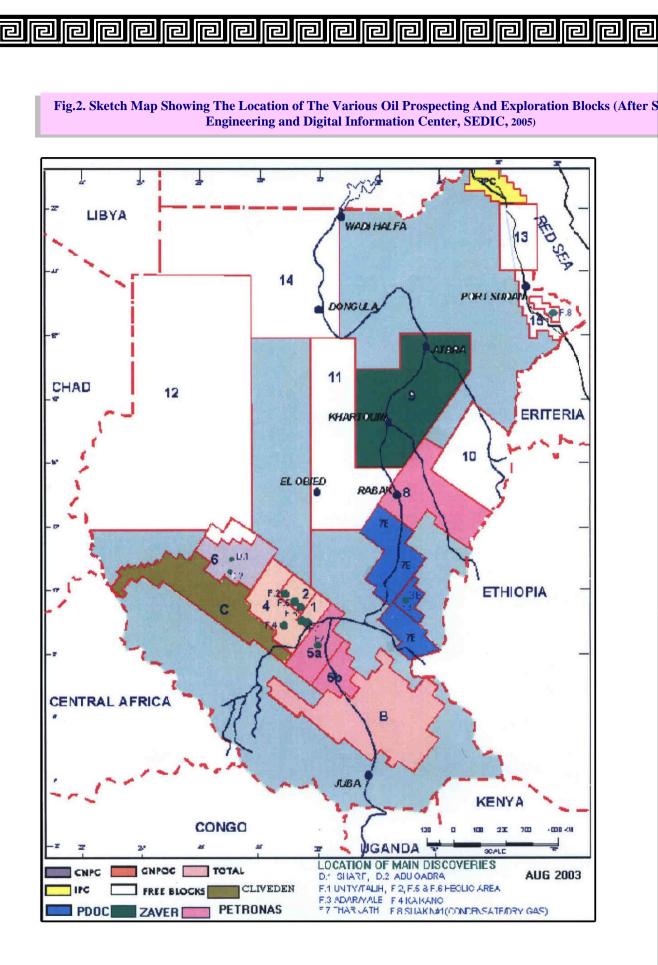
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2.4 Oil Production:

The petroleum production in Sudan began in Abu Jabra and Sharif oil fields and later in Adar-Yale and Heglig oil fields. The total production of petroleum until 1999 was over three million barrels, of which Abu Jabra and Sharif produced 471629 barrels, Adar-Yale 196347 barrels and Heglig 2517705 barrels. By the end of June 1999 the real production reached 150 thousand barrels per day from Heglig and Unity oil fields, 2004 reached 300,000 and in it barrels per day (www.sudani.co.za, htm,2002). The Government expects additional oil production from the new fields in northern and central Sudan assigned to the various companies. The Khartoum Refinery aims at upgrading the production capacity of the refining process from 2.5 million tons per year to 4.5 million tones per year by the end of 2005. The Ministry of Energy and Mining collaborated its efforts with the Refinery management in order to utilize the production of crude oil pumped from Al fullah Field, in Block 6 in order to meet the local needs for Gasoline oil, and to materialize the economical value of Alfulah

 Field. The expansion of the refinery has been supplied by a pipeline of 730 km. from Balilah field Al fullah. (Al Ray Alaam Daily, 2005)

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2.5 The Sudanese oil quality: -

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The quality of the Sudanese petroleum differs according to the field from which it is produced, but generally the most important properties can be summarized as follows (<u>www.sudani.co.za, htm</u>,2002):-

The Sudanese crude petroleum has a medium density that allows the production of economically valuable light fractions
. It contains paraffin wax, a chemical component of oil ,which makes the crude oil having a high combustion property .

• It is characterized by having small quantities of sulphur. Therefore, it is one of the best oils in the Middle East, because sulphur has harmful impact on the environment and the engines.

• It is also characterized by having the specification of the Diesel derivative above sixty octane number which is high enough to raise the burning competence.

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• However, its paraffin wax content necessitates the addition of pour point depressant in order to render the oil easily pipelined.

2.6 Energy balance in Sudan :

The whole energy consumption by the different in Sudan (agriculture, industry, domestic sectors use. transportation, commerce and services) reaches up to 6 million tons equivalent of oil per year. About 82% of this amount is obtained from firewood and charcoal, the remaining 18% of the energy budget is provided by petroleum and by both thermal and hydro-electricity, of which petroleum constitutes 16% of the energy budget (Ministry of Energy and Mining, 2000). The domestic consumption of all types of energy in houses reaches about 77% of the whole energy consumed by all other sectors (of which 90% is provided by burning the biomass).

The annual average consumption of the various, refined petroleum products during the years 1998-1994 reached about 1.5 million tons (Ministry of Energy and Mining,op.cit.) Sudan

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used to depend on imported petroleum to meet all its needs from energy from this commodity. Since 1999, the country began to use it's own petroleum. Consequently more refineries at Abu Gabra, El -Obeied , and Khartoum have been constructed together with a pipeline reaching the Red Sea Coast for export. Part of the petroleum is used in the thermal generation of electricity, which amounts to 340 mega watts out of the total electrical generation which amounts to740 mega watts (Table 2, Abdeen, 1997). A change in the energy balance is expected after the exploitation of the Sudanese petroleum, and the consequent increase in demand for the commodity in lieu of the biomass as the main source of energy. The expected demand for energy in Sudan by the end of the national comprehensive strategy (1992-2001) is shown in

Table (1).

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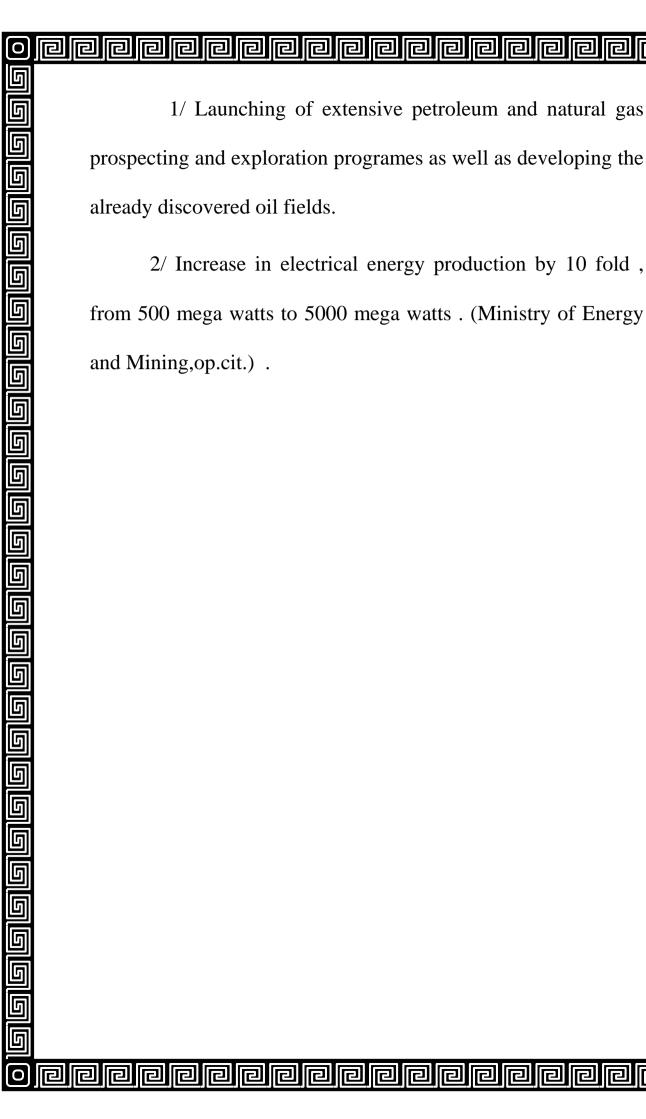
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In order to face this demand the national comprehensive strategy aimed at:-



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Table 1. Energy demand in Sudan

National Comprehensive strategy, 1992-2001

(Ministry of Energy and Mining , 2000).

STATE	THE AMOUNT
The Biomass	9 million ton equivalent oil
Oil	4million ton equivalent oil
Electricity	1.1 million ton equivalent oil
Total	14.1 million ton equivalent oil

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(Ministry of Energy and Mining , 2000).

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	National Electrical	Grid	Generation in States	Total	9
	Hydro- electric	thermal	Cities	M.W.H	9
Compound Capacity	300	340	100	740	9 G
Available Capacity	230	250	50	530] G
Potential Generated Power					5
per year				3500	5
Actual Generated Power					9
per year				2250	5
					9

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Chapter Three Analysis of Gaseous by-products and

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Pollutants in waste water at Khartoum Refinery

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Chapter Three Analysis of Gaseous by-products and Pollutants in waste water

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3.1 Gaseous by- products at Khartoum Refinery

3.1.1 Introduction :-

Khartoum Refinery Company limited (KRC) is a joint venture between the Chinese National Petroleum Corporation (CNPC) and the Ministry of Energy and Mining (MEM) of Sudan, each holding fifty percent of the shares. The joint venture agreement of the Refinery was signed in March, 1997 and the construction was officially started in May 1998. The plant was formally put into production in 2000. In this study, Khartoum Refinery at Al Gaili is taken as an example of possible pollution brought about during the processes of oil refining.

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The Refinery consists of the following production units (Khartoum Refinery Company, 2002):

Distillation Unit (CDU), capacity: 2.5 mt/y, Crude consisting of an electric desalter and crude distillation products refining.

Residual Fuel Oil Catalytic Cracking Unit (RFCC), capacity :1.8 m t/y, consisting of reaction and regeneration, distillation, absorption and stabilizatin, energy recovery, Sulphur and mercaptan removal sections

Reforming Unit, capacity: 150000 t/y and consisting of pretreatment and reforming sections.

Diesel Hydro Treating Unit (DHT), capacity: 500000 t/y, consisting of hydrogen recovery and diesel hydrogenation sections.

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Sour Water Stripping Unit ,capacity :400000 t/y.

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Utilities include : a power plant , a waste water plant , an air separation and compression unit and a river water purification plant (1500 m³/h) .

3.1.3 Refinery main production:

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The annual output is 2.2587 million tons (mt) of oil products such as gasoline, jet fuel, diesel (naphtha), fuel oil, liquefied gas (LPG), kerosene and benzene(mogas) . Among them the gasoline is unleaded, the diesel is of high quality with low sulphur , low aromatics and light colour .Due to its low Sulphur content ,Liquid Petroleum Gas (LPG) is a clean fuel satisfying the environment protection requirements.(Fig.2, KRC products Balance Flow Chart for December 2003).

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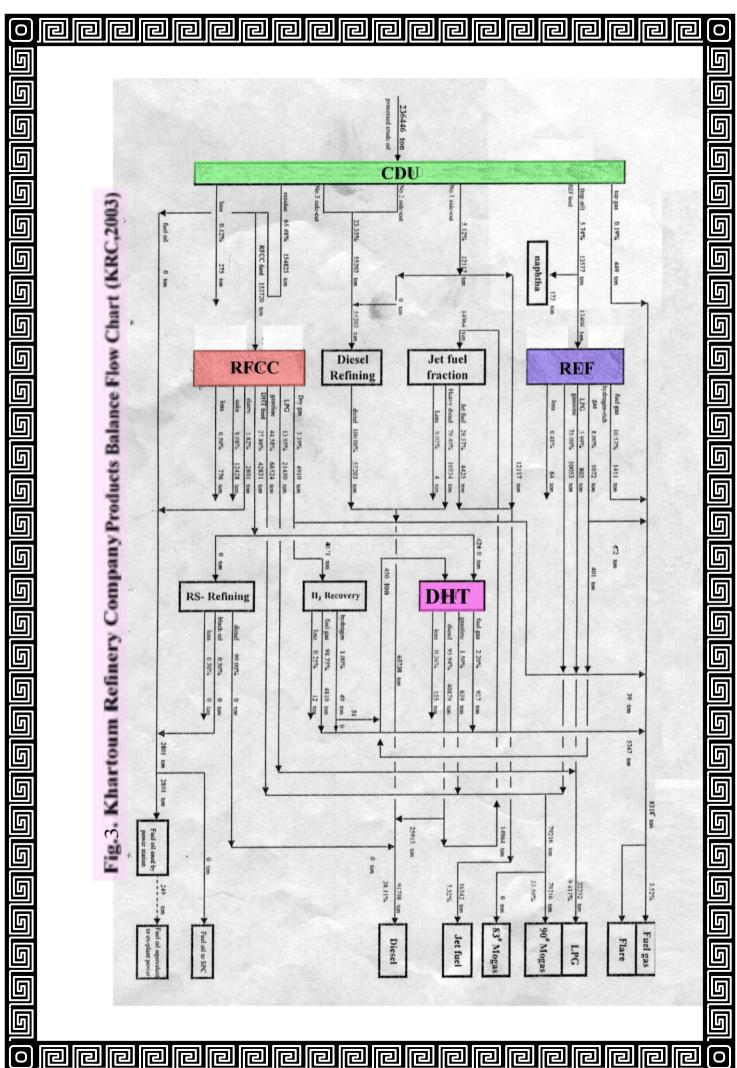
3.1.4 Air pollution (around the Refinery):

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It is expected that the Refinery can cause gaseous and liquid pollution ,bad smells and noise .The major gas pollutants include hydrocarbon vapours, nitrogen oxides, Sulphur dioxide, Sulphur trioxide, hydrogen sulphide and carbon monoxide (KRC, 2002).The major potential sources of some gaseous effluents from the Refinery are shown in Table (3).



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Deceeceece P P P Р G P P Table(3): Main gaseous effluents from the Refinery (KRC, 2002). Effluents **Potential sources** SO_2, SO_3, H_2SO_4 Combustion furnaces and boilers, H₂S flares ,catalyst regenerators heating System. hydrogen sulphide Vent from CDU ,deSulphurizer plant, waste water Hydrocarbons Flares, storage tanks, sampling operations, open effluent water separators, catalyst regenerators. Carbon monoxide Catalyst regenerators, decocking operation, motordriven compressors. Dusty materials Catalyst regenerators, combustion in boilers and furnaces, decocking. Nitrogen oxide Combustion processes, flares, catalyst regeneration Bad smelling gas Storage tanks, open waste water separators, plant sections.

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3.1.5 Waste gases analyzed and equipment used : -

 SO_2 , NO_X and CO were analyzed using the following monitor lab analyzers at Khartoum Refinery Company(KRC) :-

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- ML 9850-sulphur dioxide analyzer, USA
- Carbon Monoxide analyzer, USA .
- Nitrogen oxides analyzer, USA .

The measurements were taken during the period 20/2/2004 to 20/3/2004 when SO₂, NO_x and CO were recorded midday as average readings .

3.1.6 The results:

Table(4) shows the results of analyses of the gases SO_2 , NO_X and CO. The SO_2 values range between 0.004 mg/m³ and 0.14 mg/m³, with the majority of readings falling between 0.11 and 0.18 mg/m³. The NO_x values range between 0.001mg/m³ and 0.009mg/m³, with about 70% of the analyses ranging

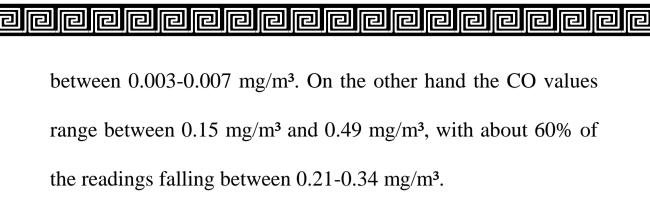


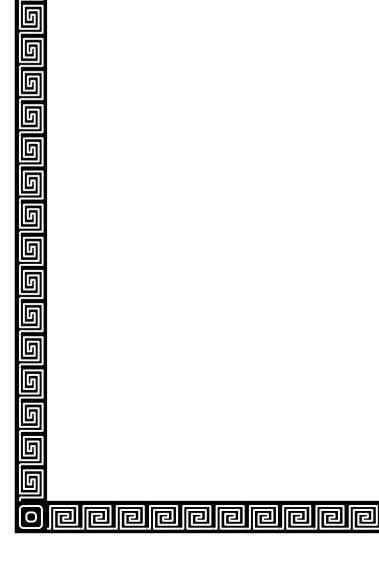
Table (4) Results of gaseous analysis using Monitor LabAnalyzers

(Readings taken mid-day)

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	Date	SO₂ mg\m³		
			NO _x mq\m³	CO mg\m³
20/2/2004		0.14	0.009	0.49
21/2/2004		0.018	0.003	0.38
23/2/2004		0.015	0.006	0.34
24/2/2004		0.016	0.003	0.18
25/2/2004		0.015	0.002	0.19
26/2/2004		0.014	0.003	0.24

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DDDC		JOCO	opope
27/2/2004			0.41
	0.013	0.003	
28/2/2004			0.34
	0.007	0.003	
2/3/2004			0.36
	0.016	0.002	
3/3/2004			0.35
	0.02	0.001	
4/3/2004			0.28
	0.022	0.003	
5/3/2004			0.33
	0.018	0.003	
6/3/2004			0.21
	0.012	0.005	
7/3/2004			0.34
	0.011	0.005	
9/3/2004			0.31
	0.015	0.005	

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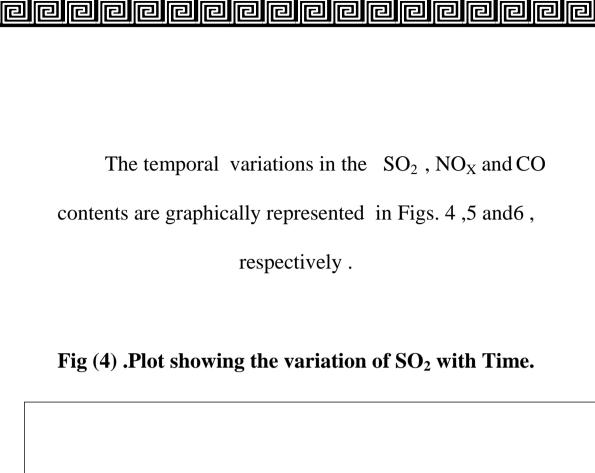
DDDC		JOOO	DDDD	ICO
	1			1
10/3/2004			0.22	
	0.021	0.004		
11/3/2004			0.19	
1.1,0,2001	0.022	0.003		
16/2/2004			0.27	
16/3/2004	0.009	0.009	0.27	
17/3/2004	0.004	0.007	0.32	
18/3/2004	0.009	0.007	0.21	
	0.009	0.007		
19/3/2004			0.16	
	0.007	0.006		
20/3/2004			0.17	
	0.013	0.007		
21/3/2004	0.01	0.006	0.15	

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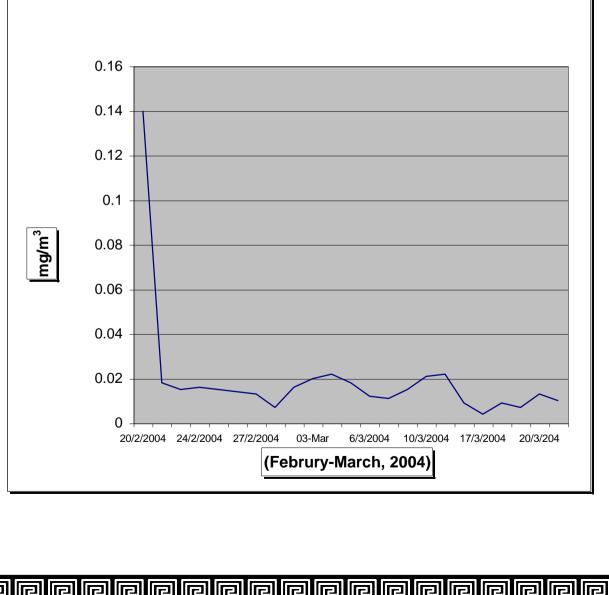
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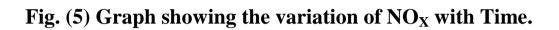
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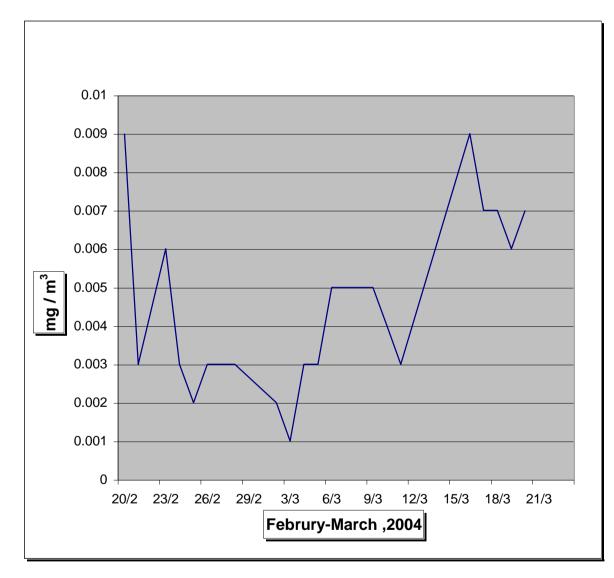
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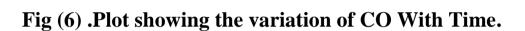
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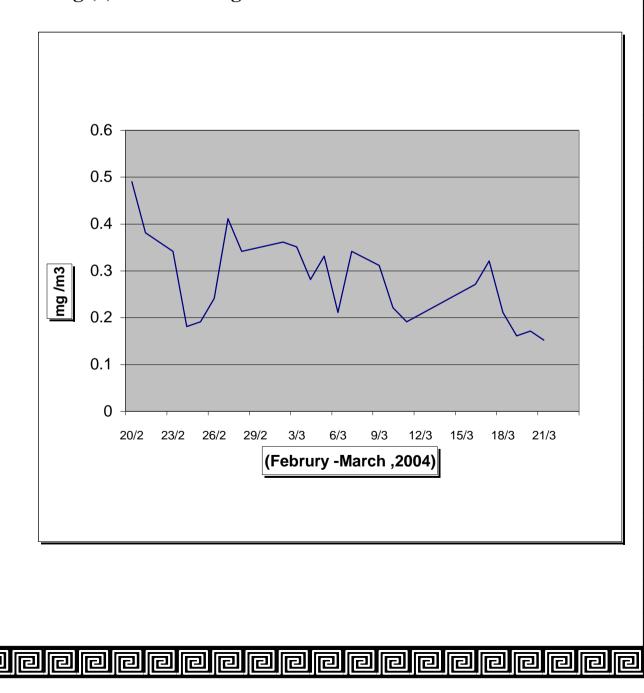
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3.2.1 Introduction :-

Waste water is one of the main liquid wastes produced during oil refining process at KRC. The waste water discharge includes waters from the following sources:-

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a-Hydro-carbon polluted waters ,i.e. processing water from oil processing units, bottom drainage from oil tanks, lab discharge, and discontinuous discharges of various utilities from polluted areas

b-The domestic sanitary water which also joins the Refinery discharge

Also ,water used in cooling or other treatment operations contains a number of organic and inorganic pollutants. Waters from the desalter and the condensed acidic water from CDU and RFCC contain sulphides , phenols, ammonia, H₂S, and different amounts of oil

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Other water pollutants include :-

-Suspended and dissolved solids.

-Biodegradable materials measured by Biological oxygen demand (BOD). —Organic matter that oxidizes with other chemicals measured with Chemical oxygen demand (COD).

In this study, the reduction of these substances practiced by the Refinery operators to permissible levels by physical, chemical and biological means is tested. This is because polluted waste waters can affect ground water, the Nile waters quality or the soil. This is brought about by:--Intoxication of water by chemicals.

-Change in the taste, odour, colour or increase in its turbidity or temperature which reduces the content of dissolved oxygen.

-Possibility of break out of fires or explosions due to the presence of hydrocarbons.

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-Chemical irritation, inflammation or chemical pneumonia. (KRC, 2002).

3.2.2 Waste water treatment plant:

Waste water treatment plant capacity=300m³/h and it consist of:-

1-Oil separator pond-1 :

It is a physical method, efficient for removing suspended hydrocarbons. The first step in the removal of hydrocarbons from water is usually by gravity separation .Through properly selected separator tanks with skimmers, most free oil and unstable oil emulsions can be separated from the water. It is the most economical way to remove large quantities of free oil from water after passing the water through large tanks to allow the phases to separate. The effectiveness of these tanks depends on the droplet size and how long the water is in the tank .Oil separator can reduce oil concentration to 2 - 25 mg/L, with an average of 15 mg/L.

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2-Floatation pond- 2 and 3 :

It is a mechanical and chemical method by using air stripping from compressors to evaporate organic compounds (VOC`s) and by adding chemicals (PAC) in order to remove dissolved hydrocarbons.

3-Bio-chemical pond -4 :

Biological treatment is used to remove low levels of dissolved hydrocarbons from wastewater streams .Biological treatment consists of mixing oxygen and nutrients with water in a tank. The bacteria then degrade the organic compounds as well as alter the chemical form of the heavy metals, sulphur, phenols, nitrogen and ammonia. This method is too slow for oil industry applications, because the high salinity of produced water inhibits the biological growth, and hence the biological treatment will

D Deleebeelee P P P not be effective in most cases. 4-

Filtration :

One way to remove oil droplets from water is to pass the water through wet filters. This method is used also to remove suspended solids. Sand or gravel filters are common media used in this process. In some special cases when the pH of waste water is too low or very high the KRC waste water treatment plant uses a system control by- pass in order to discharge the the oxidation pond without waste water to treatment (Petroleum Training Center, 2004)

3.2.3 Analysis of effluent water :

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In order to detect the type and concentration of pollutants present in the Refinery waste water, ten water samples were taken simultaneously, five from the inlet and five from the outlet of the waste water pond after treatment.

The parameters analyzed include:-

-Oil and grease.

-Sulphides

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-Phenols

- Nitrogen and Ammonia

-Total suspended solids (TSS).

- Biological oxygen demand (BOD)

- Chemical oxygen dzemand (COD).

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3.2.4 Analytical equipment:-

Following is a list of equipment used for waste water analyses at the Central Petroleum Laboratories (see Appendix –

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- UV Spectro photometer for the analyses of the sulphides,

Nitrogen and ammonia and the phenols (Plate 1).

- TSS Water Bath for the analysis of the total suspended solids (Plate 2) .
- pH Meter for the determ

ination of the pH (Plate 3).

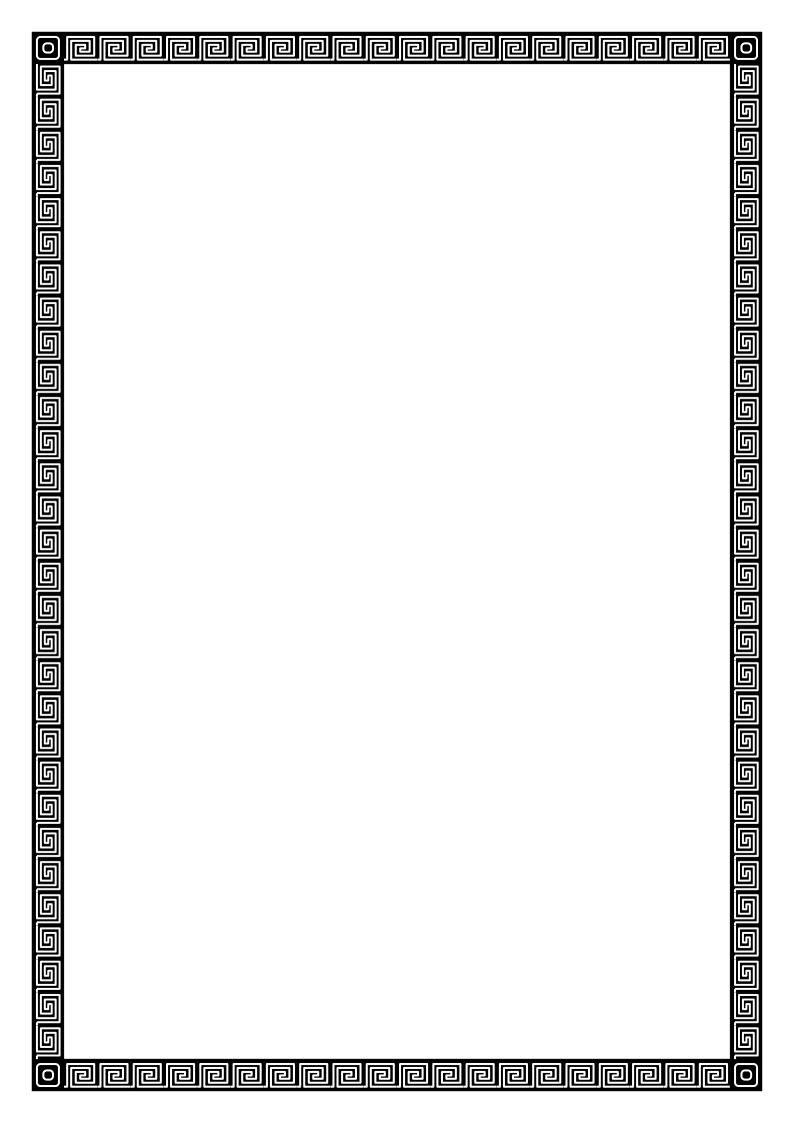
- COD Reactor measuring the chemical oxygen demand (Plate

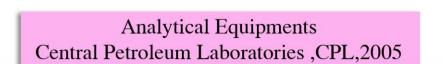
4).

- Rota Vaporate (plate 5), Soxhlet Extraction (plate 6) and the

Oven (plate 7) for the determination of oil and grease.

- BOD Incubator for measuring of the biological oxygen demand (Plate 8).





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Plate 1.UV Spectro Photometer for sulphide, nitrogn and ammonia & phenol analyses.

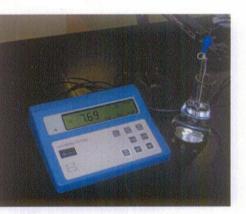


Plate 3. The pH Meter.



Plate 5. Rota Vaporate.



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Plate 2. TSS Water Bath for determination of total suspended solids.



Plate 4. COD Reacter.



Plate 6. Soxhlet Extraction.



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Tables(5) and (6) show the results of analyses of the pH sulphide, nitrogen and chemical ammonia, oxygen demand (COD), oil and grease, the total suspended solids (TSS), phenols and the biological oxygen demand (BOD) the inlet and outlet waste water, respectively. The from levels of the analyzed parameters drop as follows :- The pH from 7.15 to 4.57; the sulphide from 654.00 mg/L to 25.00 mg/L ; the nitrogen and ammonia from 47.6 mg/L to 9.96 mg/L; the chemical oxygen demand from 450.00 mg/L to 327.00 mg/L ; oil and grease from 128.40 mg/L to 10.00 total suspended solids from 183.00 mg/L to mg/L; the 32.00 mg/L; the phenols from 0.2 mg/L to 0.03; while the biological oxygen demand from 40 mg/L to 12 mg/L.

	ap				lo	DDD	D
Par	ameter	Т	Test Method	Unit		Result	
Parameter		Test Method	Ţ	Unit		Result	
pH value at 25°C	APH	A 4500 PH				7.15	
Sulphide	HACH 8	3131	ł	ıg/L		654.00	
Nitrogen and Ammonia		HACH 8038	n	ng/L		47.60	
COD	HA	ACH 8000	n	ng/L		450.00	
Oil and grease	APF	HA 5520 D		mg/L		128.40	
Total suspended solids	APł	HA 2540D		mg/L		183.00	
BOD	APH	HA- 5210B		mg/L		40.00	
Phenols	HA	CH -8047		mg/L		0.20	

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Table (5).Results of the inlet waste water analysis

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pH value at 25c	APHA 4500 PH		4.57	
Sulphide	HACH 8131	µg/L	25.00	
Nitrogen and Ammonia	HACH 8038	mg/L	9.96	
COD	HACH 8000	mg/L	327.00	
Oil and grease	APHA 5520 D	mg/L	10.00	
Total suspended solids	APHA 2540D	mg/L	32.00	
BOD	APHA- 5210B	mg/L	12.00	
Phenols	HACH -8047	mg/L	0.03	

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Table(6). Results of the outlet Waste Water analysis:

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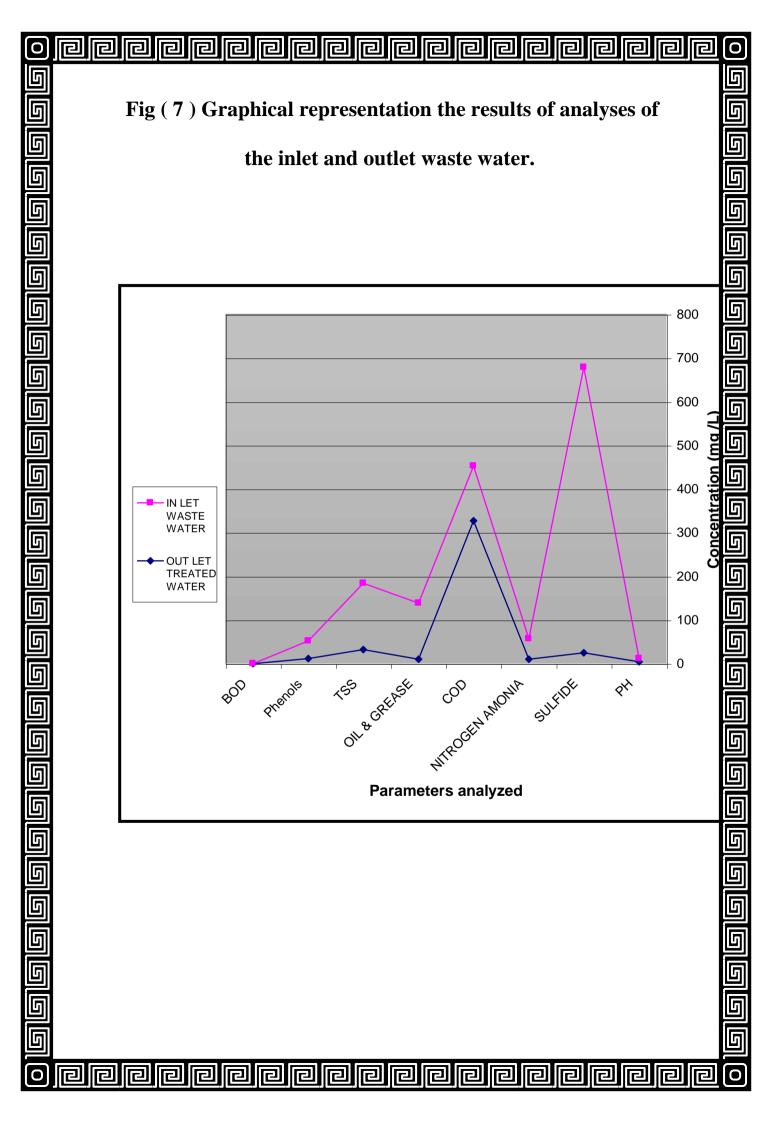
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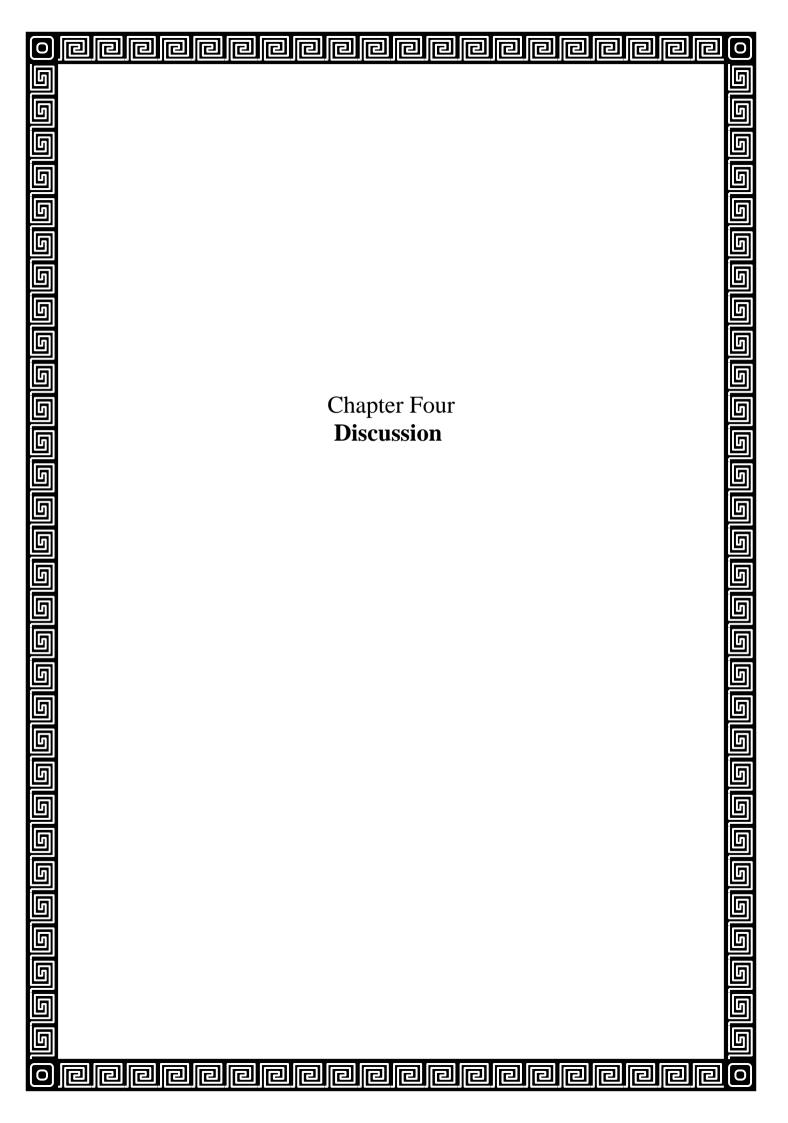
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Chapter Four Discussion

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4.1 Discussion of the results of the gaseous by- products **4.1.1 Introduction :-**

As mentioned earlier the gases SO_2 , NO_X and COliberated during petroleum distillation at Khartoum Refinery were analysed in the period from 20/2/2004 to 20/3/2004. The Chinese standards have been applied in the design construction and processing technology at the Refinery. However, the results of the analyses will be discussed in the light of the Chinese Standards, the Global Bank Guide For Air Quality and the Standard Limit For Gaseous Emissions Sudanese from petroleum refining.

4.1.2 The SO₂ gas :

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Table(4) shows the results of analyses of the gases SO_2 , NO_X and CO. The SO_2 values range between 0.004 and 0.14 mg/m³, with the majority of the readings falling between 0.11 and 0.18 mg/m³.

Comparing these results with the Chinese standards shown in Table(7), the maximum permissible limit of SO_2 emission is 0.25 mg/m³; while it is <0.04ppm in the Global Bank Guide (Table 8), and 0.36 mg/m³ in the Sudanese Standards (Table 9).

So the SO₂ emission levels are compatible with those standards and consequently, there are no serious SO₂ levels emitting from the Refinery .However, The Nile Blende Crude Oil contains about 0.04-0.06 wt % sulphur, ending up in the sour water coming from the Crude Distillation Unit overheads (CDU), Residual Fuel- oil Catalytic cracking unit Condensates (RFCC) and The Diesel Hydro Treating Unit (DHT). It is degassed as H_2S at the Sour Water Stripping Unit which has a capacity of 0.4 mt/y. The H_2S obtained is then sent straight to the flare.

4.1.3 The NOx gases :

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 NO_X values range between 0.001 and 0.009 mg/m³, with about 70% of the results falling between 0.003 and 0.007 mg/m³

Comparing these results with the Chinese standards (Table7), the maximum permissible limit of NO_x emission is 0.15 mg/m³; while it is <0.05ppm in the Global Bank Guide (Table 8) and 0.40 mg/m³ in the Sudanese Standards (Table 9). So the NO_x emission levels are compatible with those standards and consequently there are no serious levels of NO_x emitting from the Refinery . In fact , the Nile Blende Crude Oil contains only traces of nitrogen . The gas is stripped from the collected waste sour water at the Waste Water Stripping Unit where it is transformed into NH₃ gas and later mixed with water to form ammonia liquid .

4.1.4 CO gas:

CO values range between 0.15 and 0.49 mg/m³, with about 60% of the analyses falling between 0.21 and 0.34 mg/m³. Comparing these results with the Chinese standards (Table 7), the maximum permissible limit of CO emission is 6.00 mg/m³; Л

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while it is 10.00 ppm in the Global Bank Guide (Table 8) and 10.00 mg/m³in the Sudanese Standards (Table 9). So the CO emission levels are compatible with those standards and consequently, there are no serious levels of CO emitting from the Refinery. In fact, the CO gas coming from the combustion of crude oil in CDU and RFCC is burnt in the flare.

Table (10) Shows the maximum determined values for $SO_{2,}$ NO_X and CO gases for easy comparison with the Chinese Standards, Global Bank Guide and the Sudanese Standards.

Table (7). Chinese standards used for SO2, NOX and CO gases (KRC Report, 2002) :-

Hazardous limit for humans	Parameter
0.25 mg/m ²	SO ₂
0.15 mg/m ²	NO _X
6.00 mg/m ²	СО

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Table (8) Global Bank Guide for Air Quality. (KRC, 2001).

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Parameter	Hazardous limit for humans
SO _x	<0.04 ppm
NO _X	00.05 ppm (24 hrs.)
СО	10.00 ppm (8 hrs.)

Table (9). Sudanese Standards Limits Of Gaseous Emissions Resulting From Petroleum Refining (Ministry of Energy and Mining, Regulations of protection of the environment in petroleum industry, 2005):-

Parameter	Hazardous limit for humans
SO ₂	00.36 mg/m^3
NO _X	00.40 mg/m ³
СО	10.00 mg/m ³

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Table (10). Comparison of the Maximum values determined for SO_2 , NO_X and CO gases with the Chinese, the Global Bank Guide and the Sudanese Standards.

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Parameter	Maximum Value mg/m3	Chinese Standards mg/m ³	Sudanese Standard mg/m ³	Global bank guide ppm
SO ₂	0.14	0.25	00.36	< 0.04
ΝΟχ	0.009	0.15	00.40	<0.05
СО	0.49	6.00	10.00	10.00

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4.2 Discussion of the results of waste analyses:-

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The major water pollutants include : oils and grease, sulphides, phenols, ammonia, total suspended solids (TSS), biological oxygen demand (BOD) and chemical oxygen demand (COD). These parameters were analyzed in the period from 27/9/2004 to 11/10/2004 at the Central Petroleum Laboratories (CPL). (Table 5) shows the results of the analyses of the inlet waste water and (Table 6) shows the results of the analyses of the outlet treated water. The results of the analyses will be discussed in the light of the Chinese Standards and the Sudanese Standards limits of Liquid Wastes Resulting from Petroleum Refining.

As mentioned in Chapter Three, the pH values drop from 7.15 in the inlet waste water (Table 5) to 4.57 in the outlet waste water (Table 6). Comparing these results with the Chinese Standards shown in (Table11) the permissible limit of pH ranges between 6-9; while it ranges between 6-9 in the Sudanese Standards (Table 12). So the pH value in the outlet waste water indicates that the water is acidic.

4.2.2 The Sulphides: -

The sulphide values drop from 654.00 μ g/L in the inlet waste water (Table 5) to 25 μ g/L in the outlet waste water (Table 6). Comparing this result with Chinese and Sudanese standards (Table 11 and 12), it is evident that the results of the sulphides are well above those standards (1.00 mg/L), since 25 μ g/L =0.025mg/L. So the Sulphide value in the outlet treated water is compatible with those standards .

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4.2.3 The Nitrogen and Ammonia :

The Nitrogen and Ammonia values drop from 47.60 mg/L (Table 5) in the inlet waste water to 9.96 mg/L (Table 6) in the outlet waste water .Comparing this result with the Chinese Standards (Table 11), the maximum permissible limit of Nitrogen and Ammonia is 15 mg/L[;] while it is 10 mg/L in the Sudanese Standards (Table 12). So the Nitrogen and Ammonia values in the outlet treated water are compatible with those standards.

Table (11).Chinese standards used for waste watertreatment(Khartoum Refinery Company, 2002):-

Parameter		Maximum limit
pH value at 25°C		6-9
Sulphide	1	(mg/L)
Nitrogen and Ammonia	10	(mg/L)
Chemical oxygen demand (COD)	150	(mg/L)
Oil and grease	10	(mg/L)
Total suspended solids (TSS)	30	(mg/L)
Biological oxygen demand (BOD)	30	(mg/L)
Phenols	0.50	(mg/L)

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Table (12). Sudanese Limit of Liquid Waste From Petroleum Refining (Ministry of Energy and Mining, Regulations for protection of the environment in the petroleum industry, 2005).

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Parameter		Maximum limit
pH value at 25°C	6-9	
Sulphide	1	(mg/L)
Nitrogen and Ammonia	15	(mg/L)
Chemical oxygen demand (COD)	100	(mg/L)
Oil and grease	10	(mg/L)
Total suspended solids (TSS)	70	(mg/L)
Biological oxygen demand (BOD)	30	(mg/L)
Phenols	0.50	(mg/L)

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4.2.4 The Chemical oxygen demand (COD) :

The COD values drop from 450.00mg/L (Table 5) in the inlet waste water to 327.00 mg/L (Table 6) in the outlet waste water. Comparing this result with the Chinese Standards (Table 11), the maximum permissible limit of COD is 100 mg/L; while it is 150 mg/L in the Sudanese Standards (Table 12). So the COD value in the outlet treated water is not compatible with those standards.

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4.2.5 Oil and grease :

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Oil and grease values drop from128.40 mg/L (Table 5) in the inlet waste water to 10.00 mg/L (Table 6) in the outlet waste water. Comparing this result with the Chinese and Sudanese Standards (Table 11 and 12), the maximum permissible limit of Oil and grease is 10 mg/L.

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So the Oil and grease value in the outlet treated water is compatible with Chinese Standards and Sudanese Standards for water quality.

4.2.6 The total suspended solid (TSS):

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The TSS values drop from 183.00 mg/L (Table 5) in the inlet wastewater to 32.00 mg/L (Table 6) in the outlet waste water. Comparing this result with the Chinese Standards (Table 11), the maximum permissible limit of TSS 70.00 mg/L; and with the Sudanese Standards (Table 12), the maximum permissible limit is 30 mg/L.

It clear that the result of TSS is compatible with those standards.

4.2.7 The Biological oxygen demand (BOD) :-

The BOD values drop from 40 mg/L (Table 5) in the inlet waste water to 12 mg/L (Table 6) in the outlet waste water. Comparing this result with the Chinese and the Sudanese So the BOD value in the outlet treated water is compatible with those standards.

4.2.8 The Phenols:

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The Phenols values drop from 0.20 mg/L (Table 5) in the inlet waste water to 0.03 mg/L (Table 6) in the outlet treated water. Comparing this result with the Chinese Standards and the Sudanese Standards in (Table11and12), the maximum permissible limit of Phenols is 0.50 mg/L.

So the Phenols values in the outlet treated water are compatible with the Chinese standards and Sudanese Standards for water quality.

For comparison with the Chinese and Sudanese Standards, Table (13) shows the outlet values determined for pH, sulphide, nitrogen and ammonia, chemical oxygen demand (COD), Oil

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Dececececec P ٦ Р Ο Г and grease, total suspended solid (TSS), biological oxygen ந demand (BOD) and phenols. 5 Table (13). The outlet waste water values determined for pH, ٦ ٦ Sulphide, Nitrogen and Ammonia, COD, Oil and Grease, 5 TSS, BOD and Phenols for comparison with the Chinese and 5 the Sudanese Standards. واواواواواواواواواواواواواواو

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Parameter	Results	Maximum limit in Chinese standards	Maximum limit in Sudanese Standards
pH value at 25°C	4.57	6-9	6-9
Sulphide	0.025 mg/L	1 (mg/L)	1 (mg/L)
Nitrogen and Ammonia	9.96 mg/L	15 (mg/L)	10 (mg/L)
Chemical oxygen demand (COD)	327.00 mg/L	100 (mg/L)	150 (mg/L)
Oil and grease	10.00 mg/L	10 (mg/L)	10 (mg/L)
Total suspended solids (TSS)	32.00 mg/L	70 (mg/L)	30 (mg/L)
Biological oxygen demand (BOD)	12.00 mg/L	30 (mg/L)	30 (mg/L)

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Chapter Five Environmental Impact, Conclusions and Recommendations

5.1 Management of environmental hazards caused by oil refining:-

:5.1.1 Introduction

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It is claimed in the Refinery official reports (Khartoum Refining Company Report, 2000) that harmful substances such as gaseous products or in the waste water are reduced to the possible levels using physical, chemical minimum and biological means. For example:-

-Water usage is reduced by using cooling towers and water circulation.

-A sour water treatment unit is added in order to remove H₂S and NH₃ gases.

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-Water proofing of ponds by plastic sheets and construction of

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concrete paving of areas vulnerable to oil spills.

-Pollutants such as mineral oil , pH , suspended solids, NH_3 , Sulphides, COD are monitored daily, while BOD is monitored bi- weekly by the Refinery waste water analysis plant and the Health Safety and Environment (HSE) unit .

- Water from the Nile to the Refinery is a once-through system ,so that the Nile waters are not affected by any pollutants .

It is well established that the data sheets of the chemical materials used in oil refining should be delivered by the manufacturers .The data should include their physical and chemical properties, handling procedures, storage, first aid ...etc. Unfortunately, the Khartoum Refinery still lacks such information on most of the chemical materials used .

5.1.2 Gaseous Environmental Impact :

This work focuses on the gaseous pollutants, namely nitrogen oxides, sulphur dioxide, sulphur trioxide and carbon monoxide produced during oil refining at the Refinery. All the

above ,so called, green house gases pollute the atmosphere during combustion of petroleum products, whether during transportation, electricity generation or during crude oil refining . The main stream view among the scientific community is that increase in the emission of green house gases will lead to rise in global temperature beyond normal levels. Over 50% of these gases are produced from the combustion of fossil fuels .The consequences of higher temperatures will lead to gradual rise in sea level as well as in changes in global climate, which could result in the flooding of many coastal areas and disruption of various agricultural schemes (e.g. Institute of Environmental Studies, 2002).

In the following account the negative impact of these gases will be reviewed.

5.1.2.1 Carbon monoxide:

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It is a colorless, odourless gas of molecular weight 28 and specific gravity the same as that of air. Carbon monoxide affects human and animal health by combining more readily than oxygen with the haemoglobin in the red blood cells. This

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reduces the normal supply of oxygen to the body tissues. However, the resultant oxygen deficiency is reversible, but sometimes severe exposures may not be reversible.

The effect of carbon monoxide on humans is categorized as acute or chronic . Acute effects depend on the concentration of carbon monoxide, length of time of exposure, the degree of exertion and personal susceptibility.

Exposure to carbon monoxide for 10-45 minutes in a concentration of 10,000 ppm leads to unconsciousness and death. Levels of carbon monoxide concentration between 100 and 10,000 ppm for 3-15 minutes can cause headache, dizziness and nausea. At lower levels, although no obvious symptoms occur, possible effects on the central nervous system may in some cases lead to impaired vigilance or delayed reaction time (Hassan, 1981).

5.1.2.2 Sulphur dioxide :-

It is a colorless, irritant gas having a characteristic odour and taste and a molecular weight of 64.07. Sulphur dioxide concentrations of 0.3 to 1ppm can be detected by an average Decelecter individual by taste rather than odour. A concentration of 3 ppm has an easily detectable odour .Concentrations of 6-12 ppm in the atmosphere cause immediate irritation to the nose and throat .. Irritation of the eyes occurs at a concentration of about 20 ppm . If inhaled, the gas dissolves readily and affects the upper respiratory tract .In acute cases it may cause odema of the lungs and respiratory paralysis. Chronic effects on the senses of smell and taste are likely to occur on exposure for a period of over a year to variable concentrations from 30 ppm with occasional peaks of 100 ppm . The maximum permissible average concentration for ambient air three hours is 0.5 ppm, while the maximum permissible for 24 hours is 0.14 ppm; and the permissible annual arithmetic mean is 0.03 ppm (Hassan ,op.cit. 1981).

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5.1.2.3 Nitrogen oxides:-

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Nitrogen combines with oxygen to form the most common of the conventional pollutants - oxides of nitrogen (NOX).

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Indoors exposures occur because NOX is produced in unventilated rooms where gas-fires, stoves, as well as kerosene heaters are used.

In fact NOX is a threat to human and animal health as follows:-

- Exposure to high levels of NOX commonly impairs lung defenses to common infections.

- Long -term studies indicated that exposures to high levels of NO2 can lead to chronic respiratory bronchiolitis by impairing the expiratory flow rate . This effect is reversible if the level of NO2 exposure is reduced.

-Acute exposures to high levels of NO2 may cause changes within the lung that, in turn, could increase bronchial responsiveness, particularly in asthmatics.

-Any inhaled substance (including NO2) that can cause an inflammatory response, will enhance the susceptibility to allergens.

- Animals exposed to NOX are less able to ward off bacterial infections.

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- NO_X affects ozone layer. Fine particles and acids require strict controls to minimize death and serious illness. (www.healthandcleanair.org, 2003).

5.1.2.4 Acid rain :-

Fuels are composed of chemical compounds which when combusted produce exhaust gases with variable toxicity. One of these gases, sulphur dioxide, produced from the chemical reaction between sulphur (which is found in most crude oils) and oxygen , causes about 70% of what is called acid rain (e.g. Bakhiet , 1999). The rest comes from the oxides of nitrogen ,namely NO2 and NO3 , collectively called NOx . Acid rain causes lakes and rivers to become acidic . Long term increase in acid rain suffocates fish and prevents them for reproducing.

Acid rain also prevents seedlings from producing new trees. Also, it breaks down toxic metals in the ground and washes them into water sources, such as rivers. As the water becomes more acidic ,it can react with the lead and copper of water pipes , thus contaminating drinking water supplies. Moreover, acid rain damages crops, forests and their ecosystems. (Institute of <u>e de la constant de </u>

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Environmental Studies, 2002). Table (14) summarizes the negative impact of the analyzed gases on human health and the environment.

Table (14) . Negative environmental impact of the analyzed gases(KRC Environmental Report, 2000 and Bakhiet , 1999).

Effluent	Potential sources	Major effect
SO ₂ , SO ₃	Combustion furnaces and boilers , H ₂ S flares ,catalyst regenerators heating System.	 1-Human respiratory track disorders. 2-Serious losses in plants and trees. 3-metal corrosion, cracks in leather materials and paints, 4-Affects textiles
		and paper industry.
Sulphide	gas vent from CDU, desulfurizer plant, waste water.	1-Respiration problems 2-Causes drowsiness 3-Blood problems
Carbon monoxide	Catalyst regenerators, decoking operations, motor-driven compressors	Highly suffocating and when inhaled it combines with the blood haemoglobin causing oxygen starvation of tissues, especially the brain cells
Nitrogen oxide	Combustion processes , flares, catalyst regeneration	Can cause death when inhaled
Bad smelling gas(H ₂ S)	plant sections, Storage tanks, open waste-water separators.	Respiratory problems

5.1.2.5 Management of environmental hazards produced by gaseous products:-

As mentioned earlier, the major gas pollutants produced at Khartoum Refinery are nitrogen oxides(NOX), sulphur dioxide

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(SO2) and carbon monoxide(CO). The Refinery is well designed and equipped with laboratories, that monitor the waste gases continuously .In this study, an average reading at midday is given for comparison with the Chinese standards. The gas installed Refinerv detectors are all over the units for Refinery The emission instantaneous measurements. specifications are in accordance with the design demands and as well they meet the national emissions regulations.

The Nile Blende Crude Oil contains about 0.04-0.06 wt sulphur ending up in the sour water coming from the Crude Distillation Unit overheads (CDU), the Residual Fueloil Catalytic Cracking unit Condensates (RFCC) and the Diesel Hydro Treating Unit (DHT). It is degassed as H2S at the Sour Water Stripping Unit which has a capacity of 0.4 mt/y. The gas is then de-sulpherized, led up along the flare bracket to burn at the top of the flare.

The Nile Blende Crude Oil contains only traces of nitrogen. The gas is stripped from the collected waste sour water at the

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Waste Water Stripping Unit, where it is transformed into NH3

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The CO gas coming from the combustion of crude oil in CDU and RFCC is burnt in the flare.

5.1.2.6 The results of analysis of gaseous by- products:-

gas and later mixed with water to form ammonia liquid.

Table (4) shows the results of analyses of the gases SO_2 . NO_X and CO As mentioned in Chapter Three the SO_2 values range between 0.004 and 0.14 mg $/m^3$, with the majority of the readings falling between 0.11 and 0.18 mg/m³. The NO_x values range between 0.001 and 0.009 mg/m³, with about 70% of the analyses ranging between 0.003 and 0.007 mg/m³. The CO values range between 0.15 and 0.49 mg/m³, with about 60% of the analyses falling between 0.21 and 0.34 mg/m³. From the above account and comparing these results with the Chinese standards (Table 7), Global Bank Guide (Table 8) and the Sudanese Standards (Table 9) for maximum permissible limits of SO_2 , NO_X and CO emissions, we find that SO_2 , NO_X and CO levels are compatible with those standards.

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So the results of the analyses carried out clearly show the effectiveness of the treatment methods adopted by the Refinery for bringing the levels of the gases under investigation down to the permissible, harmless concentrations.

5.1.3 The environmental impact of waste water :-

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The disposal of untreated waste water produced by crude oil refining has deleterious impact on the environment such as:-

1- Toxicity of water affects human beings and other living organisms.

2- Fires and explosions are likely to occur due to the presence of hydrocarbons.

3- High temperatures affect aquatic life and reduce dissolved oxygen.

4- Colour, turbidity and taste affect the quality of natural waters, if contaminated by such waste waters.

There are three evaporation ponds constructed by the consultant group of Khartoum University (2001) in order to receive the waste water (Table 15):-

Table (15): Evaporation pond dimensions and activityvolumes

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Area of pond	650x420	m²
Depth	2.2	m
Pre-treatment effluent	460	m³/h
Daily discharge	11000	m ^{3.}
Estimated evaporation area	800000 .	m ^{2.}
Estimated evaporation loss	6800	m³/day
Daily excess water	4200	m³

Embankments 3m high were constructed around the ponds on natural soil level without proper lining. Plastic sheets were spread on the bottom of the ponds to prevent soil pollution.

The excess water could be utilized in forest plantation and a Refinery green belt with an area of 100 feddans . However, the project was rejected for security reasons.

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A waste water plant was added at Khartoum Refinery in order to treat the waste water for reuse in industrial or other activities .Also, the treatment protects surface and underground water from pollution.

Pollutants such as mineral oil, pH, total suspended solids (TSS), nitrogen and ammonia, sulphides and chemical oxygen demand (COD) are monitored daily. The biological oxygen demand (BOD) is monitored bi- weekly by the Refinery waste water analysis plant and by the Health Safety Environment (HSE) laboratories. Mechanical, chemical and biological means are used in the waste water treatment plant to decrease the pollutants to the minimum possible level.

5.1.5 The results of waste water analyses:-

Tables(5) and (6) show the results of analyses of the pH, sulphide, nitrogen and ammonia, chemical oxygen demand, oil and grease, the total suspended solids, phenols and the biological oxygen demand from the inlet and outlet waste

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water. The levels of the analyzed parameter drop as shown on Table (16) below.

Table (16). The Results of parameters analyzed in wastewater from inlet and outlet treatment pond .

				<u> </u>
Parameter	Unit	Results of Inlet waste water	Results of outlet waste water	والك
pH value at 25°C		7.15	4.57	G
Sulphide	μg/L	654.00	25.00	<u>5</u> 5
Nitrogen and Ammonia	mg/L	47.60	9.96	<u>SS</u>
COD	mg/L	450.00	327.00	5 5 5
Oil and grease	mg/L	128.40	10.00	5
Totalsuspendedsolids (TSS)	mg/L	183.00	32.00	اکلک
BOD	mg/L	40.00	12.00	5 S
Phenols	mg/L	0.20	0.03	S S
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Comparing these results with Chinese Standards (Table 11), and the Sudanese Standards limits of Liquid Wastes Resulting from Petroleum Refineries (Table 12), we find that:

1) The pH value in the outlet waste water indicates that the water is acidic and not suitable for drinking purposes.

2) The chemical oxygen demand (COD) value, in the outlet treated water is not compatible with those standards.

3) The oil and grease; the phenols; the total suspended solids (TSS); the nitrogen and ammonia; the sulphide and the biological oxygen demand (BOD) values in the outlet treated water are compatible with the Chinese and the Sudanese Standards for treated water quality. The outlet treated waste water is not suitable for drinking, but it can be used in the evaporation pond for raising fish, plantations and cooling of engines. It is clear from the analyses carried out in this study that the methods

adopted by the Refinery are ineffective in bringing the levels of

5.2 Conclusions:-

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Crude oil refining was started in Khartoum Refinery by the end of June 1999. The actual production of oil refining reached 50 thousand barrels per day. The Khartoum Refining Company expects additional oil refining to reach 100 thousand barrels/day by the end of 2005. This study focuses on the control and management procedures of the harmful by-products of oil refining adopted by the Refinery. The gaseous by- products analyzed include SO2. NOX and CO. The waste water pollutants analyzed include the pH, oil and grease, sulphides, phenols, nitrogen and ammonia, the total suspended solids (TSS), the biological oxygen demand (BOD), and the chemical oxygen demand (COD).

The results of the analysis of the gaseous- by products : (Table 4, Chapter Three) were found to be compatible with the Chinese standards (Table 7), Global Bank Guide (Table 8) and

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the Sudanese Standards (Table 9). Hence, the results clearly show the effectiveness of the treatment methods adopted by the Refinery for bringing the levels of the gases under investigation down to the permissible, harmless concentrations.

The results of analyses of the pollutants in waste water are shown in Table (16). When compared with the Chinese Standards (Table11), and the Sudanese Standard limits of Liquid Wastes Resulting from Petroleum Refineries (Table 12), it is clear that oil and grease; phenols; nitrogen and ammonia; the total suspended solids (TSS); the sulphide and the biological oxygen demand (BOD) values in the outlet treated water are all compatible with those standards. However, the analyses carried out in this study show that the methods adopted by the Refinery are ineffective in bringing the levels of the pH and the chemical oxygen demand to the permissible, harmless concentrations.

So it is clear that the control of these parameters is not effective and needs revising. Also, the discharge of these polluted waters on the ground depending on its rocky nature around the Refinery does not exclude the presence of fractures

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in these rocks that would render them permeable. Hence, the possibility of contamination of any water underground can not be ruled out completely. Furthermore, the manner by which the chemicals used in oil refining are stored also needs revising. The package of recommendations suggested in this study is likely to alleviate most of the present deleterious environmental impact

5.3 Recommendations:-

Petroleum as an energy source is indispensable in our modern life of today despite the hazardous by-products expected from oil refining. Yet, some precautionary measures should be adopted in this industry. The Refinery efforts to reduce SO_2 ; CO; NO_X ; Oil and grease; phenols; nitrogen and ammonia; the total suspended solids (TSS); the sulphide and the biological oxygen demand (BOD) values are quite successful. But, the levels of the chemical oxygen demand are still high and the pH values are low (acidic) and are unacceptable by the international standards. Therefore, the writer suggests the following recommendations in order to alleviate the hazardous impact of these parameters:-

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1. Data sheets of the chemical materials used should be available at the Refinery.

2. Disposal of the waste water on the rocky ground around the Refinery is not hundred percent safe .Because hard basement rocks might contain underground water if affected by faulting. Therefore , geophysical investigation around the Refinery should be carried out to detect any presence of faulting in the area, which might help the seepage of the polluted waters into underground waters.

3-Possibility of the extraction and marketing of some useful elements in liquid waste water.

4- Annual medical check-up of the KRC employees should be adopted.

5-Raising the awareness of the KRC staff as well as associates on site, about environment protection, is of prime importance.

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6-Use of waterproof lining of tank basins, concrete pavements, evaporation ponds and all areas where oil spills may occur, is essential in order to prevent oil seepage.

7-Modernization of some of the analytical equipments is necessary.

8-Periodic investigation of the part of the pipe line at the bottom of the river in order to detect, in good time any faults that might lead to oil leakage into the river water.

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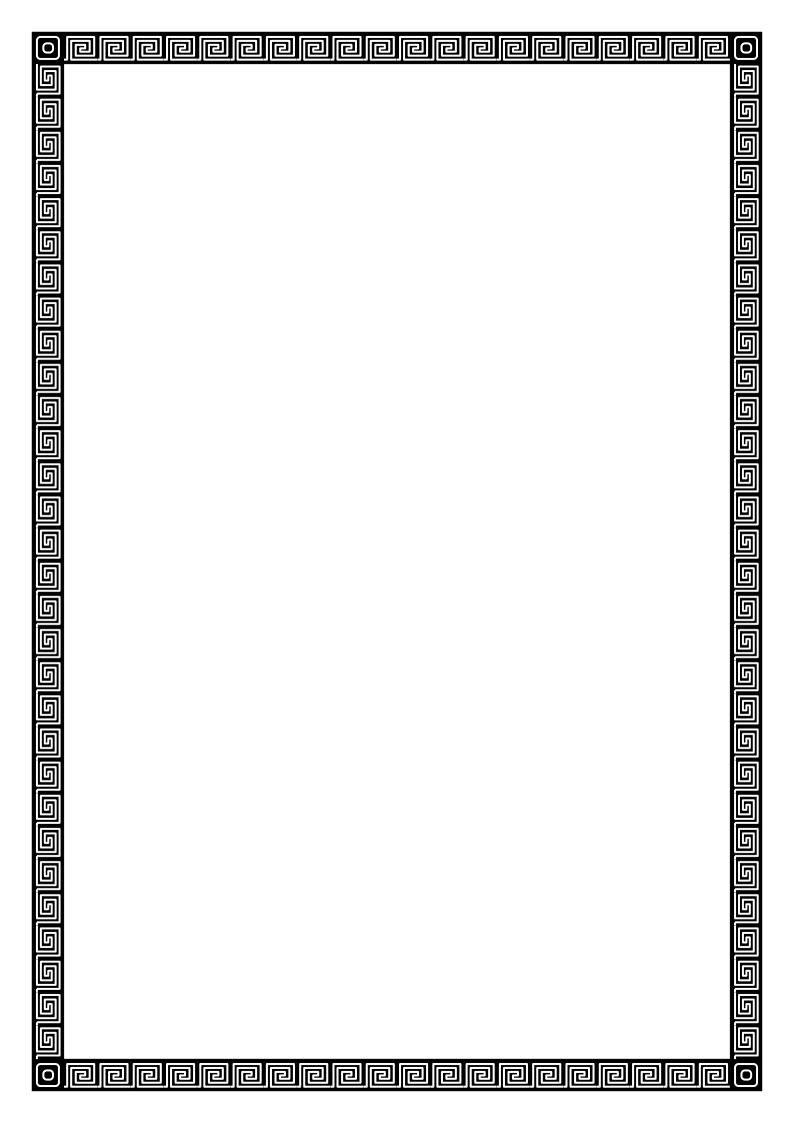
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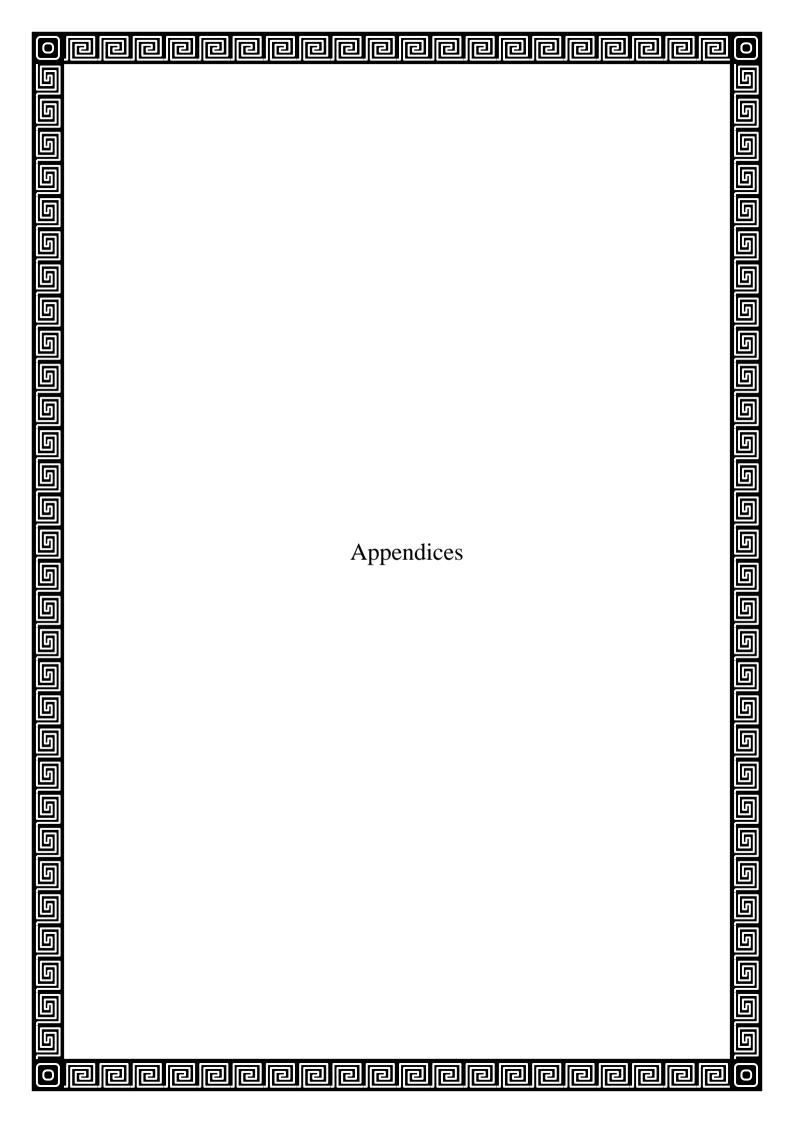
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1. The Analysis of the Sulphide by Methylene Blue Method:-

The analysis is fully computerized. First the HASH PROGRAM is selected and the number 3500 for the sulphide analysis is entered and the ENTER key is pressed so that the display showed: HACH PROGRAM:3500 Sulphide, with the wavelength(λ),665nm, is automatically selected.25 mL from the sample were measured into a sample cell and 25 mL of deionized water were transferred into a second sample cell (the To each cell 1.0 ml of Sulphide 1 Reagent was added blank). and whirled in order to mix. 1.0 ml of Sulphide 2 Reagent was added to each cell. Then, A5- minute reaction period was stored by pressing the soft key under START TIMER. When the timer beeped, the blank sample was placed in the cell holder and the light shield closed .Then the soft key under ZERO was pressed and the display showed $0\mu g/L S^{2-}$. Finally, the prepared sample

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The soft key under HACH PROGRAM was pressed and the stored program for low range ammonia nitrogen (NH₃-N) was selected by pressing the number 2400 and the ENTER key was pressed so that the display showed: HACH PROGRAM :2400N, Ammonia Nessler , with the wavelength(λ), 425nm , is automatically selected. A 25-mL mixing graduated cylinder was filled (the prepared sample). Another 25 ml mixing graduated cylinder was filled with deionized water (The blank). Three drops of polyvinyl Alcohol Dispersing Agent were added to each cylinder by holding the dropping bottle vertically. The cylinder was inverted several times to ensure proper mixing. Then 1.0 ml of Nessler Reagent was pipetted into each cylinder Stopper and inverted several times to ensure proper mixing. Next, the soft key under START TIMER was pressed so that a

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one-minute reaction period began. Each solution was poured into a sample cell. When the timer beeped the blank sample was placed into the cell holder and the light shield closed. Then the soft key under ZERO was pressed and the display showed: 0.000mg/L NH₃. Finally, the prepared sample was placed into the cell holder then the light shield closed. The results in mg/L ammonia expressed as nitrogen (NH₃-N) (or chosen units) were taken.

3.The analysis of the Phenols :

The analysis is also fully computerized. First the HACH PROGRAM was selected and the number 2900 for phenols analyses was entered and the ENTER key was pressed . The display showed HACH PROGRAM 2900 phenols, with the wavelength (λ)460 nm is automatically selected. Then 300 mL from the deionized water were measured into 500mL graduated cylinder and the measured deionized water was transferred into a 500ml separatory funnel (the blank). 300mL of sample were measured into a 500 ml graduated cylinder. Then the

Decelerection P P Ο ភា ٦ prepared sample was transferred into another 500 ml separatry وهووه ومووو ومووو ومووو ومووو ومووو funnel and 5ml of hardness 1 buffer to each separatory funnel were added and stoppard and shaked in order to mix. Then the contents of one phenol reagent powder pillow were added to each separatory funnel, stoppard and shaked in order to dissolve. Then the contents of one phenol 2 reagent powder pillows were added to each separatory funnel, stoppard and shaked in order to dissolve. 30 ml of chloroform were added to each separatory Then each funnel was inverted funnel, stoppard. temporarily vent, and vigorously shaked for 30 seconds. Then the stoppers was removed in order to allow both funnels to stand until the chloroform settles to the bottom of the funnel. A large pea-sized cotton plug was inserted into the delivery tube of each funnel. The chloroform layers were drained into separate sample cells (one for the blank and one for each sample). Then the blank sample was placed into the cell holder and the light shield closed. Then the soft key under ZERO was pressed and the display showed: 0.000 mg/L phenol. Finally, the prepared 5 ٦

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sample was placed into the cell holder and the light shield closed. The result in mg/L phenols was taken.



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4. Determination of the Total Suspended Solids:-

A disk with its wrinkled side up was inserted into the filtration apparatus under vacuum and washed with three successive 20-mL portions of reagent-grade water. The suction was continued in order to remove all traces of water. Then the vacuum was turned off, and the washings discarded. The filter was from the filtration apparatus and transferred into an inert aluminum weighing dish. The crucible and filter were then dried in an oven at 103 to 105 °C for 1 h. To measure the volatiles the crucible was ignited at 550 °C for15 min in a muffle furnace, then cooled in a desiccator and weighed . The cycle of drying, igniting, cooling, desiccating, and weighing was repeated until a constant weight is obtained or until the weight change is less than 4% of the previous weight or about 0.5 mg, whichever less, and the crucible was stored in a desiccator until needed.

A sample volume to yield between 2.5 and 200 mg was chosen and the residue dried residue . If the volume filtered fails to meet the minimum yield, the sample volume was

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increased to 1L. If complete filtration takes more than 10 min, then the filter diameter was increased or the sample volume decreased.

Sample analysis : Assemble filtering apparatus and being suction. The filter was wetted with a small volume of reagent and the sample was stirred with a magnetic stirrer at such a speed to shear larger particles, (if present) to obtain a more uniform (preferably homogeneous) particle size . Centrifugal force may separate point of sample with drawal is varied. While stirring, pipet a meas-samples, piped from the approximate midpoint of container but not in vortex. A point both mid depth and midway between wall in vortex was chosen. The filter was washed with three successive 10 ml volumes of reagent-grade water and allowed to drain completely after each washings. Suction was continued for about 3 mints after filtration is complete. Samples with high dissolved solids may require additional washings. The filter was then carefully removed from the filtration apparatus and transferred to an aluminum weighing dish as a support. Alternatively, the crucible and

P Ы filter were removed complete from the crucible adapter. If a Gooch crucible was used the sample was dried for at least 1 h at 103C° to 105 C° in an oven and cooled in a desiccator to weighing temperature. The cycle of drying, cooling, desiccating and weighing was repeated until a constant weight is obtained or until the weight change is less than 4% of the previous weight or within 0.5 mg, whichever is less. About 10% of all samples were analyzed twice. Duplicate determinations should agree within 5% of their average weight if the volatile solids are to be determined. The residue was analyzed according to the programme 2540E.

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Calculations:

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total suspended solids mg / L =

(A-B)X1000

sample volume (mL)

where:

A(mg) = weight of filter + dried residue, and B(mg) = weight of filter.

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5. pH value:-

Instrument calibration: In each case follow manufacture's instructions for pH meter and for storage and preparation of electrodes for use. Solutions for short-term storage of electrodes 4000 have conductivity greater than µmhos /cm. was recommended. Tap water is a better subsume than distilled water but pH 4 buffers is the best for the single glass electrode and saturated KCL was preferred for a calomel and AG/AGCL reference electrode. Saturated KCL is the preferred solution for a combination electrode. Then electrodes wet by returning them were kept to storage solution whenever pH meter is not in use.

Before use, electrodes from storage solution were removed, rinsed and blotted dry with a soft tissue then placed in initial buffer solution and that is the potential point. Next a second buffer within 2 pH units of sample pH was selected and the sample and buffer were brought to the room temperature, such as 25°C, or the temperature of a fresh sample. The electrodes were removed from first buffer, rinsed thoroughly with distilled water, blotted dry and immersed in second buffer. The temperature of measurement was recorded and adjusted temperature dial on meter so that meter indicates pH value of buffer at test temperature.

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The pH value listed in the tables was used for the buffer used at the test temperature. Then electrodes from second buffer were removed , rinsed thoroughly with distilled water and dried electrodes as indicated above and immersed in a third buffer below pH 10, approximately 3pH units different from the second; when only occasional pH measurements were made and the instrument was stable , standardized less frequently .

analysis: equilibrium electrodes Sample between was sample established and stirred insure homogeneity; to conditioned electrodes after cleaning by dipped them into sample for 1 min. blotted dry, immersed in a fresh portion of the same sample, and read pH. .

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6. <u>Chemical Oxygen Demand (COD) determination by</u>

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Calorimetric Measurement Method (for 0 to 40 mg/L range).

100 mL of sample were homogenized for 30 seconds in a blender. The COD Reactor was turned on preheated to 150 °C. The plastic shield was placed in front of the reactor. The cap of the COD Digestion Reagent vial was removed for the appropriate range and held at 45-degree angle in order to pipette 2.00mL (0.2 mL)for the 0 TO 15,000 mg/L range) of sample into the vial. The cap of the vial was replaced tightly and the COD vial was rinsed with deionized water and wiped with a clean paper towel. Next the vial was held by the cap and over a sink , inverted gently several times to mix the contents and replaced in the preheated COD reactor. A blank sample was prepared by repeating steps 3 to 6, substituting 2.00 mL (0.2 mL for the 0 to 15,000 mg/L range) with deionized water and placed the blank in the COD reactor. The vials were then heated for 2 hours. Afterwords, the reactor was turned off and the vials were left for 20 minutes to cool to 120 °C or less, inverted

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The sample was digestion described for the "Oxygen Demand determination . The key under HACH PROGRAM was pressed and the program number for ultra low range COD was selected by pressing 2700 with the numeric keys followed by ENTER . The display showed : HACH PROGRAM :2700 COD ,ULR with the wavelength(λ ,350 nm) was automatically selected. Then the N Tube Adapter was inserted into the sample module by sliding it under the thumb screw into the alignment grooves and then fastened with the thumb screw. The outer surface of the blank was cleaned with a towel, and placed into the adapter with the Hach logo facing the front of the instrument the light shield closed. The soft key under ZERO was and pressed and the display showed: 0.00mg/L COD. The outer surface of the sample vial with a towel. Finally, the sample vial was placed into the adapter with the Hach logo facing the front of the instrument and the light shield closed. The results in mg/L COD (or chosen units) was then displayed.

7. Determination of Oil and Grease:-

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The sample bottle was marked at the water meniscus. Then 1:1 HCL or1:1 H₂SO₄ was added to pH 2 or lower (5ml for 1L). Next the sample was transferred to a separatory funnel by liquid funnel and the sample bottle was rinsed with 30 mL extracting solvent and the solvent washings were added to the separatory funnel. The bottle was shaken vigorously for 2 min until the layers separated. The aqueous layer and a little amount of organic layer were drained into the original sample container. The centrifuged material was transferred into an appropriate separatory funnel and the solvent layer was drained twice through a funnel with a filter paper with an additional 10g of Na₂SO₄ solvent-rinsed. Then aqueous layers and any remaining emulsion or solids were added together into a separator funnel. Then twice 30ml solvent was extracted each time. The solvent in the flask was distilled in a water bath at 85°C for either solvent The solvent was collected in an ice-bath-cooled system.

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receiver. After the visible solvent condensation stops, the flask was removed from the water bath. Still at 85°C, air was drawn through the flask for 15 min with an applied vacuum for the last 1 min. The sample was then cooled in a desiccator for at least 30 min and weighed. Finally, the sample volume was calculated by the difference from the initial volume.

8.Determination of the Biological Oxygen Demand (BOD)

The water sample was heated to within 20° C of its incubation temperature (typically200°C,680F). Then a clean graduated cylinder was used to pour the correct sample volume into a BOD Trak sample bottle. The sample dilutions for more information on BOD range selection.

Selection of Sample Volume

BOD Range(mg/L)	Required Volume (mL)
0-35	420
0-70	355

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0-350	160
0-700	95

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Next a 3.8-cm(11/2-inch) magnetic stir bar was placed in each sample bottle. The contents of one BOD Nutrient Buffer Pillow were added to each bottle for optimum bacteria growth. Then Stopcock Grease was applied to the seal lip of each bottle and to the top of each seal cup. After that a seal cup was placed onto the neck of each bottle. Then the funnel was used and the contents of one Lithium Hydroxide powder pillow was added to each seal cup .The lithium hydroxide particles were not allowed to fall into the sample. The bottle was placed on the chassis of the BOD Trak. The appropriate tube was connected to the sample bottle and the cap was firmly tightened .Each tube was tagged with the channel number, and the channel number setup was reflected on the control panel. The instrument was placed in the incubator and started (The electrical plug was connected and turned on). All stir bars were rotating. If a stir bar slided to the side of the bottle off the unit it was gently replaced. The channel should not be started until the stir bar was rotating

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oppersent the second sec ٦ properly. To select a test duration, the<(left) and the>(right) arrow keys were pressed simultaneously and held until the time menu appears and the CHANNEL6 key was pressed to activate the test length parameter. Then the arrow keys were used to choose a5-,7-,or10- day test(test length is shown on the last line of the screen) .The OFF button was pressed to save the selections and exit the menu. To start a test the channel number corresponding to the bottle was pressed and then the ON key. A menu for selecting the BOD range was displayed. For 0-350 mg/L range, the>(right) key was pressed once . For 1-700mg/L the >key was pressed for a second time. For 0-35 mg/L range, the <(left)key was pressed once . For 0-70 mg/L the<key was pressed for a second time. The ON key was pressed and held to start a test. A graph was displayed .To cancel a test, press OFF. The BOD results were read directly from the BOD Trak display by pressing the key corresponding to each sample. Finally, a brush and hot soapy water were used to clean all the bottles, stir bar, and seal cups and they were then rinsed thoroughly with distilled water.

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