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Crude oil salts in petroleum refining.

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UNIVERSITY OF LOUISVILLE

CRUDE OIL SALTS IN PETROLEUM REFINING

A Dissertation

Submitted to the Faculty

Of the Graduate School of the University of Louisville

In Partial Fulfillment of the

Requirements for the Degree

Of Master of Science

Department of Chemistry

By

Thomas Porter Bailey

Year

1947

NAME OF STUDENT: THOMAS PORTER BAILLY

TITLE OF THESIS: CRUDE OIL SALTS IN

PETROLEUM REFINING

APPROVED BY READING COMMITTEE COMPOSED OF THE
FOLLOWING MEMBERS:

NAME OF DIRECTOR: DR. G. C. VERNON

DATE: May 12, 1947

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T. P. B.

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CRUDE OIL

CRUDE OIL SALTS IN PETROLEUM REFINING

It is well known that crude oil is a complex mixture of hydrocarbons, varying from Methane, the simplest hydrocarbon, to compounds of very high molecular weight. Sulfur, oxygen and nitrogen are usually present in moderate quantities. It is stated by Gruse and Stevens¹⁷ that "hundreds of analyses of samples of petroleum from all over the world agree strikingly in indicating a carbon content of 85 to 87 percent, hydrogen from 11 to 14 percent, with oxygen, nitrogen and sulfur in amounts varying from traces to 2 or 3 percent". This constancy of composition is considered remarkable in view of the fact that many crude oils, while fitting above elementary analyses, have widely varying physical properties. Mayberry¹⁷ explained the constancy of composition on the basis that any given crude oil consists of only a few homologous series of hydrocarbons. Variations in the amount of each series present accounts for the difference in physical properties of the crude oils, but makes relatively little difference in the elementary composition.

Crude oil may be described, in a qualitative way, as a liquid, ranging in color from transparent brown through brownish green to black, having specific gravity ranging from 0.81 to 0.985 and boiling from 75 to above 700° F. It is generally highly inflammable.

Upon subjection to fractional distillation and other refining and manufacturing processes it yields gasoline, kerosene, distillates, lubricating oils, fuel oils and numerous by-products. The U. S. Bureau of Mines has issued numerous analyses of crude oils produced throughout the world. The following are typical:^{21,29,20}

Sample 23397
Pepher well no. 1
1,194-1,214 feet
W. E. Pepher

Parker Field
Third Sand
R.I. 3385(p27)²¹

Item 17
Pennsylvania
Butler County

GENERAL CHARACTERISTICS

Specific gravity, 0.795
Sulphur percent, 0.12
Saybolt Universal viscosity at 100°F., 38 sec.

A.P.I. gravity, 46.5
Color, light green

DISTILLATION, BUREAU OF MINES HEMPEL METHOD

Dry distillation

Barometer 747 mm. First drop: 85°C. (185°F.)

Temperature, °C.	Per- cent cut	Sum, per cent of cut	Specific gravity	A.P.I. Viscosity of cut at 100°F.	Cloud test, °F.	Temperature, °F.
Up to 50						Up to 122
50 - 75						122 - 167
75 - 100	7.3	7.3	0.661	73.3		167 - 212
100 - 125	8.9	16.2	.724	63.9		212 - 257
125 - 150	8.9	25.1	.741	59.5		257 - 302
150 - 175	7.5	32.6	.756	55.7		302 - 347
175 - 200	6.8	39.3	.770	52.3		347 - 392
200 - 225	5.4	44.8	.780	49.9		392 - 437
225 - 250	5.8	50.6	.790	47.6		437 - 482
250 - 275	7.4	58.0	.804	44.5		482 - 527

Vacuum distillation at 40 mm.

Up to 200	4.5	4.5	0.829	39.2	41	25	Up to 392
200 - 225	5.0	9.5	.830	39.0	46	40	392 - 437
225 - 250	3.6	13.1	.843	36.4	61	65	437 - 482
250 - 275	5.1	18.2	.851	34.8	77	75	482 - 527
275 - 300	3.0	21.2	.860	33.0	98	90	527 - 572

Carbon residue of residuum 1.2 percent; carbon residue of crude 0.2 percent.

APPROXIMATE SUMMARY

	Percent	Sp.gr.	A.P.I.	Viscosity
Light gasoline	7.3	0.691	73.3	
Total gasoline and naphtha	39.4	0.736	60.8	
Kerosene distillate	18.6	.793	46.9	
Gas oil	8.2	.830	39.0	
Nonviscous lubricating distillate	12.0	.853- .861	38.4-32.8	50-100
Medium lubricating distillate	1.0	.861- .863	32.8-32.5	100-200
Viscous lubricating distillate	-			Above 200
Residuum	18.7	0.887	28.0	
Distillation loss	2.1			

	Item 9	
Celmar-Plymouth Field		Illinois
Hoing sand	Sample 35135	McDonough County
439-507 feet	R.I. 3532(pll) ²⁹	4N-4W-4th

GENERAL CHARACTERISTICS

Specific gravity, 0.845	A.P.I. gravity, 36.0°
Sulfur, percent, 0.57	Color, greenish-black
Saybolt Universal viscosity at 77°F., 54 sec.; at 100°F., 43 sec.	

DISTILLATION, BUREAU OF MINES HEMPEL METHOD

Distillation at atmospheric pressure, 743 mm. First drop, 41°C.(106°F.)

Fraction No.	Cut °C.	at °F.	Per-cent	Sum, per-cent	Sp. Gr., 60/60°F.	°A.P.I. 60°F.	C.I.	S.U. visc., 100°F.	Cloud test, °F.
1	50	122							
2	75	167	1.5	1.5	0.837	74.5	-		
3	100	212	4.2	5.7	.699	70.9	11		
4	125	257	6.3	12.0	.728	62.9	16		
5	150	302	5.5	17.5	.747	57.9	18		
6	175	347	5.1	22.6	.764	53.7	19		
7	200	392	4.8	27.4	.780	49.9	20		
8	225	437	5.2	32.6	.796	46.3	22		
9	250	482	5.6	38.2	.810	43.2	23		
10	275	527	6.9	45.1	.824	40.2	25		

Distillation continued at 40 mm.

11	200	392	2.8	47.9	0.844	36.2	31	41	20
12	225	437	6.1	54.0	.848	35.4	29	45	35
13	250	482	5.9	59.9	.861	32.8	32	57	50
14	275	527	5.8	65.7	.875	30.2	35	85	65
15	300	572	5.5	71.2	.888	27.9	38	150	80

Residuum	27.9	99.1	.953	17.0
----------	------	------	------	------

Carbon residue of residuum, 8.8 percent; carbon residue of crude, 2.4 percent.

APPROXIMATE SUMMARY

	Percent	Sp.Gr.	°A.P.I.	Viscosity
Light gasoline	5.7	0.696	71.8	
Total gasoline and naphtha	27.4	0.741	59.5	
Kerosene distillate	17.7	.811	43.0	
Gas Oil	8.4	.848	35.4	
Nonviscous lubricating distillate	10.6	.853- .878	34.4-29.7	50-100
Medium lubricating distillate	7.1	.878- .894	29.7-26.8	100-200
Viscous lubricating distillate	-	-	-	Above 200
Residuum	27.9	.953	17.0	
Distillation loss	0.9			

East Texas Field
Woodbine sand, Upper Cretaceous
3,762-3,791 feet

Item 27
Sample 39300
R.I. 3699(p21)²⁰

Texas
Rusk County
F. Cordova Survey

GENERAL CHARACTERISTICS

Specific gravity, 0.830
Sulfur, percent, 0.29
Saybolt Universal viscosity at 100°F., 41 sec.

A.P.I. gravity, 59.0°
Color, greenish black

DISTILLATION, BUREAU OF MINES HEMPEL METHOD

Distillation at atmospheric pressure, 745 mm. First drop, 32°C.(90°F.)

Fraction No.	Cut °C.	at °F.	Per-cent	Sum, per-cent	Sp. Gr., 60/60°F.	°A.P.I. 60°F.	G.I.	S.U. Cloud visc., test, 100°F. °F.
1	50	122	3.6	3.6	0.836	91.0	-	
2	75	167	3.3	6.9	.835	91.3	5.1	
3	100	212	5.6	12.5	.714	66.7	18	
4	125	257	6.7	19.2	.741	59.8	22	
5	150	302	5.8	24.8	.761	54.4	24	
6	175	347	5.6	30.4	.781	49.7	27	
7	200	392	3.9	34.3	.796	46.3	28	
8	225	437	4.3	38.6	.809	43.4	28	
9	250	482	5.1	43.7	.823	40.4	30	
10	275	527	6.4	50.1	.834	38.2	30	

Distillation continued at 40 mm.

11	300	592	4.0	54.1	0.852	34.6	35	41	20
12	225	437	5.8	59.9	.853	33.4	34	47	40
13	250	482	4.8	64.7	.875	30.2	38	60	65
14	275	527	4.6	69.3	.882	28.9	39	89	80
15	300	572	5.6	74.9	.892	27.1	40	155	98

Residuum 21.8 96.7 0.968 14.7

Carbon residue of residuum, 10.5 percent; carbon residue of crude, 2.3 percent.

APPROXIMATE SUMMARY

	Percent	Sp.Gr.	°A.P.I.	Viscosity
Light gasoline	12.5	0.679	76.9	
Total gasoline and naphtha	34.3	0.734	60.0	
Kerosene distillate	9.4	.817	41.7	
Gas oil	14.6	.846	35.8	
Nonviscous lubricating distillate	9.6	.862-.884	32.7-28.6	50-100
Medium lubricating distillate	7.0	.884-.897	28.6-26.5	100-200
Viscous lubricating distillate	-	-	-	Above 200
Residuum	21.8	.968	14.7	
Distillation loss	3.3			

It is general knowledge that crude oils are obtained from subterranean deposits. Just how they were produced originally is still a matter of theory, but geologists have spent considerable time in studying the types of geologic formations in which the oils are found, and such information has been quite useful in locating new sources. The oil is obtained by drilling wells which range in depth from 100 feet to more than two miles. Recently a few wells have been drilled to three miles in depth. From some wells the oil flows by subterranean pressure, but most wells have to be pumped, at least within a short time after oil is struck.

The United States is the foremost producer of crude oil in the world. Venezuela is second and Soviet Russia is presumed to be third. The following tabulation published in 1946 by The Petroleum Publishing Company, Tulsa, Oklahoma gives latest production and refining figures:¹²

WORLD PRODUCTION AND CAPACITY OF REFINERIES

(1,000 bbl. daily)

Country	Production	Refining Capacity	
		Crude charge	Cracking
North America:			
Canada	21	245	78
Cuba	1	4	2
Mexico	129	152	14
United States	<u>4,800</u>	<u>5,300</u>	<u>3,150</u>
Subtotal	4,951	5,701	3,244
South America:			
Argentina	62	94	56
Bolivia	1	1	0
Brasil	1	7	0
Chile	0	1	0
Colombia	60	17	0
Ecuador	6	2	0
Peru	32	28	7
Trinidad	55	75	30
Uruguay	0	6	2
Venezuela	1,100	124	55
Aruba & Curacao	<u>0</u>	<u>560</u>	<u>240</u>
Subtotal	1,517	915	370
Europe - excl. Russia:			
Austria	20	16	0
Belgium	0	11	4
British Isles	1	111	20
France	1	44	15
Germany	15	(*)	(*)
Hungary	12	12	1
Italy	1	4	7
Netherlands	1	18	12
Poland	2	21	2
Portugal	0	6	0
Romania	85	100	25
Sweden	0	4	3
Yugoslavia	0	5	0
Miscellaneous Europe	<u>3</u>	<u>10</u>	<u>0</u>
Subtotal	142	362	89
Russia	(*)	(*)	(*)

WORLD PRODUCTION AND CAPACITY OF REFINERIES (cont'd)

(1,000 bbl. daily)

Country	Production	Refining Capacity	
		Crude charge	Cracking
Middle East:			
Egypt	26	37	6
Iran	422	402	123
Iraq	96	7	0
Kuwait	30	0	0
Palestine	0	0	0
Qatar	(✓)	0	0
Saudi Arabia (Bahrein)	<u>196</u>	<u>200</u>	<u>15</u>
Subtotal	770	709	179
East Indies:			
Borneo	}		
Java			
Sumatra		55	63 (*)
Ceram		—	—
Subtotal	35	63	(*)
Far East:			
Burma	2	(*)	(*)
China	1	1	0
India	7	10	5
Japan	<u>4</u>	<u>13</u>	<u>(*)</u>
Subtotal	14	24	5
Australia	0	6	1
Miscellaneous	<u>1</u>	<u>1</u>	<u>0</u>
Subtotal	1	7	1
World total excl. Russia	7,230	7,781	3,888
**Russia (est.)	<u>500</u> /	—	—
Grand Total	7,730	7,781	3,888

*Data unavailable due to conditions resulting from war. / Shut in.

**Based on pre-war figures. Oil and Gas Journal, December, 1946.

CRUDE OIL SALTS

In addition to the normal components of crude oils, there are usually contaminants with which the oils have come in contact. Such foreign materials consist principally of dirt, brines, acids and crystalline salts. The brines are made up of naturally occurring salts and all the foreign material is held in the oils by emulsion or mechanical suspension. The emulsions are stabilized by emulsifying agents present in the oil. The principal salts are chlorides and sulfates of sodium, calcium, iron, and magnesium. A table of typical analyses of salts in crude oils is given by the Petroleum Rectifying Company of California: 30

TYPICAL ANALYSES OF CRUDE CHARGING STOCKS

(Salt Concentrations in Pounds per Thousand Barrels (ptb) of Crude Oil)

State	Field	Gravity Deg. API	Water Pct.	Chlorides ptb. as NaCl	Sul- fates ptb. as Na ₂ SO ₄	Calcium plus Magnesium ptb. as NaCl
Texas	Duggan-Slaughter	31.8	0.06	191	8.5	151
	Midland	32.7	1.1	114	n.d.	n.d.
	Ector County	34.5	0.1	104	12.0	28.4
	East Texas	27.9	0.2	44	Trace	16.0
Arkansas	Schuler	33.7	0.2	45	3.8	17.8
	Sour Schuler, Jones					
	Sand	33.3	0.4	138	3.0	57
	Sweet Schuler, Mixed	37.6	0.2	105	11.7	43
California	Wilmington	21.4	0.2	59	n.d.	n.d.
	Santa Maria	15.5	0.7	110	1.0	19.3
	Dominguez	29.5	1.5	151	Trace	18.7
	Ventura	28.2	2.0	239	22.4	56
Oklahoma	(Chiefly Wilcox Sand)	41.3	0.2	81	4.2	19.2
Kansas	West Kansas	37.2	0.1	124	10.0	30.0
Michigan	West Branch	32.3	0.1	141	10.8	45.5
Illinois	Illinois	36.9	0.1	55	8.6	30.6
Wyoming	Oregon Basin	19.9	0.6	13	22.4	20.0
Canada	Vermilion	15.2	1.0	305	Trace	84
	Lloydminster	15.4	3.0	865	Trace	174
	Turner Valley	42.4	0.08	45	8.6	51
U.S.S.R.	Buguruslan	28.5	1.1	300	2.0	41
	Buguruslan	29.2	0.4	201	37.0	26
	Nebetdae	32.3	1.6	155	58.0	20
	Syzran	25.9	1.3	494	260	131
	Ishimbay	27.0	0.7	436	7.0	79
Egypt	Ras Charib	18.4	2.4	1,035	4.0	165
Mexico	Pesa Rica	30.1	0.2	69	50	39
Argentina	Cachenta	29.8	2.0	525	n.d.	n.d.
	Mendoza	26.3	1.2	150	n.d.	n.d.
Trinidad	"Middle Octane" Crude	23.1	0.7	56	1.0	9

(n.d. -- not determined)

PROBLEM
AND
OBJECTIVES

PROBLEM

Salts in crude oil cause fouling and corrosion of heat transfer and fractionating equipment.

During the development of petroleum processing methods, refiners have become increasingly aware of the damaging effects of the salts present in crude oils. Such damages take the general forms of fouling and corrosion of the heat-transfer and fractionating equipment. The problem is so serious in many cases as to cause highly uneconomical operation of refineries.

OBJECTIVES

The objectives of this thesis are to assemble data regarding the inorganic salts in crude oil; their distribution in the products therefrom; and their deposition and action on petroleum refining equipment.

EFFECT OF SALTS
ON REFINERY EQUIPMENT

Effect of Salts on Refinery Equipment

In general when salts are deposited in various units of refineries, clogging, hot spots and tube blistering are the principal results. Deposition is usually most severe in heat transfer equipment or at any point where there is rapid heat input or a slow rate of evaporation. The Bureau of Mines states that rapid corrosion occurs in condenser lines, heat exchangers, still tubes, cracking coils, fractionating towers, in both topping and cracking operations when crude oils of high salt content are processed.⁷ This fact has been confirmed by practically all refineries. Generally the most severe corrosion is noted at points of steam and vapor condensation. If the temperature is high and the water is wholly in the vapor stage, the corrosion due to salt is much less pronounced. At higher temperatures the corrosion is largely due to other causes, according to most technologists. Sulfur compounds are generally regarded as the corrosive agents at high temperatures. However, according to Puckett^{8,6}, who analyzed products of corrosion, the principal corrosion at high temperatures is due to free acid and chloride salts found in crude oils. He states that the chloride salts of calcium and magnesium hydrolyze to produce free hydrogen chloride that establishes an oxidation-reduction cell with hydrogen sulphide and iron. Davis, Jones and Neilson¹¹ state that ferrous chloride is produced by the reaction of HCl on the iron. The ferrous chloride is then acted upon by hydrogen sulphide to liberate more HCl which again attacks the iron. Another opinion is that the hydrogen sulphide forms first and is then attacked by the HCl to liberate more hydrogen sulphide and thus complete the vicious cycle. Egloff and

associates¹⁴ suggest that corrosion encountered in cracking stills is due to hydrated salts of calcium and magnesium chlorides that probably melt in their own water of crystallisation and hydrolyse, producing hydrochloric acid. They also state that the greater the HCl produced from a given crude oil, the greater the formation of hydrogen sulphide during the refining process.

The decomposition of calcium and magnesium chlorides to form hydrochloric acid during distillation is illustrated by the accompanying graphs. These graphs were published by The Petroleum Rectifying Company along with the following comments: (Fig. 1 and 2)

"For magnesium chloride the curves show the influence of both concentration and the type of oil in which the salt is dispersed. The stability of Mg_2OCl_2 has led to the conclusion that the hydrolysis of Magnesium chloride proceeds according to the following scheme:

If acidic materials are present - as may be the case in crude oil but not in white oil - the hydrolysis may be expected to undergo a second step such as:

X represents the negative radical of an acid of moderate strength. The crude oil sample must have contained sufficient acidic materials to cause 90% hydrolysis of the magnesium chloride when the concentration was 10 ptb but not sufficient to react with 100 ptb quantitatively. The lack of acidic materials in the white oil probably accounts for the decreased hydrolysis."

It will be noted from the curves showing the hydrolysis of calcium chloride that the percent decomposed at a given temperature is considerably less. However, since there is usually a great deal more

DECOMPOSITION OF MAGNESIUM CHLORIDE

Fig. 1

DECOMPOSITION OF CALCIUM CHLORIDE

Fig. 2

calcium than magnesium present, the contribution of the quantity of the calcium to the total amount of acid formed must not be overlooked.

It may be stated then with reasonable accuracy that in a pure oil system such as white oil, at the distillation temperature of 650° F., the hydrolysis of sodium chloride is negligible, calcium chloride is about 2 percent and magnesium chloride is about 50 percent.

In a crude oil the hydrolysis is generally much higher and should be determined by actual distillation. (A common method is described elsewhere in this thesis.) It is possible to have alkaline materials present that might reduce the evolution of hydrochloric acid so the actual distillation with steam is the best method of measuring the corrosive character of a given crude oil. It may be further stated that at higher temperatures encountered in cracking furnaces the degree of hydrolysis may be expected to increase. The quantity of hydrogen sulfide formed during distillation, illustrated by the charts, was not determined. However, it is known that the quantity of H_2S formed during distillation is related to the total amount of sulfur compounds present in the crude oil. It is thought that there may be some relation between the quantity and character of salts present and the amount of hydrogen sulfide which will be evolved. The theory exists that when hydrogen sulfide and hydrogen chloride exist simultaneously in a distillation system, the corrosion is much greater than when HCl is present in the absence of H_2S .³⁴

Davis, Jones, and Neilson¹¹, in their studies on the relationship of hydrogen chloride release to salt content, found that sodium chloride, either alone or with magnesium chloride, proved to be inert. Calcium chloride showed virtually no hydrogen-chloride release when distilled alone in concentrations up to 200 pounds per 1,000 barrels of oil. In

the presence of magnesium chloride, the calcium chloride, up to a concentration of 30 pounds per 1,000 barrels, gave no hydrogen chloride release, the two salts apparently having no effect on each other. However, calcium chloride seemed to suppress the hydrolysis of magnesium chloride when the calcium chloride was present in concentrations of 200 pounds per 1,000 barrels with magnesium chloride. Magnesium chloride alone definitely hydrolyzed and released hydrogen chloride. At concentrations below 5 pounds per 1,000 barrels the results indicated that the magnesium chloride completely hydrolyzed, while at a concentration of 150 pounds per 1,000 barrels the hydrogen chloride release was 45 pounds, which is equivalent to 39 percent complete hydrolysis of the salt.

The quantity and kinds of salts that may remain in the crude oil without causing any harmful effects will vary for each refinery system and for each crude oil charged. Due to the complexity of the corrosion problem of various refineries, conditions that prove satisfactory to one system might prove unsuitable to another. Thus, Hanson¹⁸ states that corrosion of cracking equipment will occur when combined calcium and magnesium chlorides exceed an estimate of 25 pounds per 1,000 barrels of charging stock. The Petroleum Rectifying Company²³ states that no corrosion is expected when the total magnesium and calcium chloride content is less than 10 pounds per 1,000 barrels. East Texas refiners reported to Foster¹⁶ that magnesium chloride and calcium chloride begin to decompose to form hydrogen chloride and magnesium oxide at 300° F., and that the deposition of salt in tubes is eliminated when the salt content is reduced to 40 pounds per 1,000 barrels, although severe corrosion still occurs.

REFINING METHODS

Before taking up refining methods, a word of explanation may be in order. The effect of salts upon any refining process is closely related to the design and complexity of the plant. In order to properly study the problem, in a general way, it was decided to illustrate, and discuss briefly, common types of refineries ranging from the simplest to the most complex. Since specific study was to be given to the process of Astma Oil Company, it was considered necessary to illustrate it also and give some of the most important effects of salts experienced within recent years.

REFINING - OLD METHODS

Early refining methods were principally of the batch distillation type, characterized by the schematic diagram which follows:¹⁰ In these processes a given amount of crude oil was charged into a shell still (Fig. 3) and distillation begun. The stills were generally without fractionating columns and separation of components was poor. It was customary to distill off a gasoline fraction, with direct fire under the still, having an end point up to 457° F. After the gasoline fraction, steam was sometimes used for the remainder of the distillation or it was run without steam if desired. The kerosene fraction was next collected having an end point around 550° F. and followed by a gas oil fraction or fractions depending upon the type of products desired. The residuum was used as fuel oil, lubricating oil stock or distilled until coke formed. The type of crude oil being processed generally governed the types of final products produced.

In these methods the salts deposited on the bottom of the stills and caused blistering and inefficient heat transfer. The condenser, run-down lines and roofs of tanks were seriously corroded due to HCl if the salt content of the crude oil was high. If exchangers were used to pre-heat the crude oil, deposition of salts was heavy.

The residue products were probably the only ones affected by the presence of salts. For asphalt or lubricating oil stock, the marketing specifications were difficult to meet at times.

The early methods of cracking heavy gas oils into lighter products were similar in design to the batch distillation equipment, with the exception that a series of oil circulation tubes were added.¹⁵ These tubes were connected beneath the shell still in the firebox or so located that more heat was applied to them than to the shell. These

OLD METHOD - CRUDE OIL REFINING
(Skimming Distillation)
Fig. 3

stills were usually kept under low pressure during the distillation, and during the first part of the run, new charging stock was gradually added as the first products of cracking were removed. As these stills operated on a distillate, no salt troubles were encountered, but considerable difficulty resulted from coke deposition on the bottom of the shell which caused still bottoms to be burned out frequently. These stills were superseded rapidly by the tube stills wherein all the heating of the oil is accomplished while the oil is being circulated in the tubes which are enclosed within a furnace.

Assuming that most of these stills were operated for cracking purposes and were charged with a distillate oil, any troubles due to fouling and corrosion, or any effect upon products quality, were due to causes other than salts.

A schematic diagram of the shell and tube combination follows:
(Fig. 4)

OLD METHOD - CRUDE OIL REFINING
(Cracking Distillation)
Fig. 4

REFINING - NEW METHODS

In making the transition from the old methods to the new methods in refining, no attempt has been made to trace the development through intermediate stages. The development of the refining industry has been closely paralleled to that of the automobile. A number of schematic diagrams follow which illustrate present day processes of various leading types. It is obvious from these diagrams that the shell still has been superseded by the pipe still and a modern refinery is a complex and integrated installation. The modern pipe stills are generally high temperature, high pressure, heating units depending upon the type of products desired. If only straight run products are desired the temperature must be lower than if highly cracked materials are desired. If lubricating oils are required the heavier residues are distilled in vacuum, in order to produce distillates of higher boiling points and higher viscosities.²⁴ (Fig. 5 and 6)

Just prior to and during the recent World War the major development in refining was directed toward the catalytic processes. These processes differ from the conventional thermal cracking plants in that some provision is made for contacting the oil vapors of the fraction to be cracked with a catalyst mass. The catalysts are finely divided silica and alumina in various combinations, and often containing oxides of Ca, Mg and Fe. The refineries employing catalysts are of two general types:

1. The fixed-bed type as the Houdry process.²⁵ (Fig. 7)
 2. The moving-bed processes as the Thermoform and²⁵ (Fig. 8)
- Fluid Catalyst types.²⁷ (Fig. 9)

In the former, the catalyst is contained in a reaction chamber and

LUMMUS TWO STAGE DISTILLATION UNIT

LUMMUS THREE STAGE DISTILLATION UNIT

Fig. 6

HOUDRY CATALYTIC CRACKING PROCESS

Fig. 7

THERMOFOR CATALYTIC CRACKING PROCESS

Fig. 8

FLUID CATALYTIC CRACKING PROCESS

Fig. 9

the oil vapors are passed through. At least two catalyst cases are required so that one may be regenerated while the second is being used for cracking. The moving-bed processes move fresh catalyst to the reaction chamber for the cracking operation and then move it out again for regeneration. The Thermoform process employs mechanical elevators for this while the Fluid Catalyst process employs air or gases to "fluff up" the catalyst mass and thereby cause it to move to and from the reaction and regeneration zones as a "fluid". The Thermoform and Fluid Catalyst Processes are the foremost processes in the production of catalytically cracked gasolines, naphthas, and light fuel oils. It should be remembered that catalytic cracking is more expensive than thermal cracking but the octane number of the gasoline produced is superior to thermally-cracked gasolines. The need for higher octane number gasolines during the recent war motivated large expenditures for catalytic cracking plants which are now finding use in preparing superior gasolines for civilian consumption. It should also be kept in mind that catalytic cracking plants are designed for operation in conjunction with a topping plant or perhaps a topping plant and a thermal cracking plant as well. This is generally the most economical procedure.

The effect of salts on modern refining equipment is probably less pronounced than on the older processes as alloy metals are employed in exchangers, still tubes and condensers if the corrosion is anticipated in advance. The problem of plugging of exchangers handling crude oil is serious as modern exchangers employ small tubes with high coefficients of heat transfer. Even a small deposition of salt might be serious. Desalting of the crude oil is most desirable. Deposition of coke in still tubes will occur more rapidly than normal if salt content of

crude oil is heavy; and, of course, the corrosion of condensers will be a problem.

The effect on products is probably negligible in most cases. If asphalts or heavy lubricating oils are being manufactured, the problem of meeting marketing specifications may be difficult.

REFINING - METHOD OF AETNA OIL COMPANY

The refining process of Aetna Oil Company may be described as a combination topping and thermal cracking operation. A shell still of the older methods is used in series with a more modern tube still which serves as a thermal cracking plant. The crude oil enters the system through two heat exchangers - one being exhaust steam to crude oil and the second being residual fuel oil to crude oil - which raise the temperature to around 212° F. Prior to the exchangers the crude oil is mixed with 3 to 7 percent of water for desalting purposes. After being heated the crude and water are further emulsified by a ten-pound pressure drop across an emulsifying valve. It then passes to the four Petresco Desalters where the emulsion is broken and most of the salt removed. From the desalters the crude passes to a shell still and the temperature raised to 350° F. by gas and fuel oil burners. A light gasoline distills from the shell still through a small fractionator. The crude then passes through another heat exchanger, heated by hot gases from the cracking plant, and flashed to an evaporator which allows the remainder of the gasoline, as well as the kerosene and diesel fuel to pass out the top as a vapor and to a second fractionator which divides the outs. The topped crude is then cracked in a tube still into gasoline, light distillate fuel oil and residual fuel oil; all of which are separated by one evaporator and two fractionators. All gases generated by the process are consumed in heating the stills and boilers. The remainder of the heat is supplied by burners using residual fuel oil from this process. A diagram of the Aetna Process follows: (Fig. 10)

Legend

□ = Pump
 E = Heat Exchanger
 F = Fractionator
 A = Accumulator
 1,2,3,4 = Desalters

Simplified Flow Diagram

AETNA OIL COMPANY, INC.

Louisville, Kentucky

Fig. 10

Prior to the installation of desalting equipment at Aetna Oil Company, excessive fouling due to salts was experienced in the residual fuel oil exchanger which preheats the crude oil. Considerable corrosion was evident in the condensers handling the straight run gasoline as well as the run-down lines handling this material. The tops of the storage tanks for the gasoline also corroded rapidly. Excessive corrosion was often experienced in the top trays of the straight-run fractionator.

In the cracking operation a great deal of trouble was experienced with the condenser for cracked gasoline. There was much evidence of quantities of HCl in the condenser. It was customary to use ammonia gas to counteract this corrosion and same was injected into the topped crude oil before it entered the cracking furnace. If sufficient ammonia was used to react with all the HCl there were excessive deposits of ammonium chloride in the condenser which prevented it from functioning properly. Periodic injections of water were made to wash out the ammonium chloride but this was quite troublesome and because the condenser could not properly cool the gasoline considerable quantities of this product were lost as gas, which would have been marketable if recovered. The deposits of ammonium chloride also restricted the flow of gasoline sufficiently at times to cause back-pressure on the fractionator, which is undesirable. Due to inaccurate control methods for the injection of ammonia, the HCl was not all neutralized much of the time and corrosion was often pronounced.

The tendency of still tubes and high-temperature exchanger tubes to "coke up" was often pronounced and in many cases this could have been due to salts in the oil.

It is well to keep in mind that fouling and corrosion, especially in high temperature operations, cannot always be attributed entirely to salts but rather to a combination of salts, sulphur compounds and oxygen compounds. However, it is known that petroleum cokes taken from tubes and evaporators usually contain a sizeable percentage of salts and it is presumed that a salt crystal could serve as a nucleus about which coking could readily occur.³³

Pumps handling hot oils containing quantities of salts are often scored and corroded excessively. A marked improvement has been noted in some of the pumps at Astra Oil Company since desalting has been practiced.

It is generally assumed that salts do not materially affect distillate products. It has been stated that certain gasolines will have greater response to tetraethyl lead if the crude oil is desalted before refining but this was not true of the gasolines produced at Astra Oil Company. As far as is known, the salts present in the crude oils, at Astra Oil Company, had no effect upon the distillate products. The salts concentrated in the residual fuel oil, but as the percentage was quite small, no noticeable difficulties were reported. It is known that the ash content of the residual fuel oil is now less than one-half as great as it was prior to desalting. Since the ash content is due mostly to salts, such a decrease was to be expected. These salts are no doubt deposited on refractories within furnaces, but it is doubtful if any difficulties would result from this deposition.

DESALTING METHODS

DESALTING METHODS

With the advent of difficulties due to salts, petroleum engineers began to develop methods for counteracting the difficulties. Desalting was the most logical solution to the fouling problem, supplemented by the use of ammonia gas and alloy metals for counteracting corrosion. The most important desalting methods which have been developed commercially are:²

Electrical Precipitation

Simple Washing and Settling

Heat and Pressure

Chemical Treatment

Contact with a Solid

The electrical processes are based upon the same fundamental principle which has been stated by Allison¹, to the effect that when a crude oil and brine emulsion is subjected to an electric field of high potential, the dispersed droplets assume positive and negative charges which attract each other and cause coalescence. In actual practice the crude oil is emulsified with 8 to 20 percent of water and heated to about 200° F. and passed between horizontal electrodes made of concentric rings. Approximately 30,000 volts is maintained across the electrodes which breaks the emulsion and causes the water to separate, taking with it about 90 percent of the salts present. The Petroleum Rectifying Company, Los Angeles, California, has the foremost process in this group.

The washing and settling processes are self-explanatory. Due to their inefficiencies they are not very widely used except with the addition of heat and pressure to break the emulsions. The pressure does not materially assist with the emulsion breaking but it prevents vaporization of the crude oil. Many of the heat and pressure processes also employ a chemical additive which further assists in breaking the emulsions. These chemicals have been divided into groups by Dow¹³. In general they are chemicals which react with the emulsion droplets in some manner which will cause the droplets to rupture or coalesce.

The most recently developed processes are based upon contacting the crude oil emulsions with some solid material which causes surface tension changes and separation of the principal part of the water and salts. Some of the solid substances which have been used⁸ are sand, excelsior, finely-divided glass, alumina and others. An investigation using fine glass fibers has been reported by the A. & M. College of Texas¹⁹, and pilot plants using glass fibers have been installed at Standard Oil Company, Whiting, Indiana.²²

EXPERIMENTAL

ANALYTICAL METHODS

METHOD FOR EXTRACTING SALTS FROM OILS ³¹

The principle of this method is to thoroughly emulsify the crude oil, diluted with benzene to decrease its viscosity, with a water-acetone extractant, then to remove the water or aliquot portion thereof by settling or centrifugation, titrating the water-acetone extract with standard silver nitrate. The end point was recorded by a potentiometer using a standard calomel cell versus a silver-button electrode. (The Mohr or ^{38,37} Volhard methods for chlorides can also be used but with less certainty of end-point). When the sample is 200 ml, the water 171 ml, the acetone 25 ml, the benzene is 100 ml, (the benzene merely dilutes the oil and does not enter the calculations), the silver nitrate .05N, and 100 ml aliquot of the extract is titrated; the burette reading times 10 gives the pounds of sodium chloride per 1000 barrels of crude oil. Assuming thorough emulsification, (20 to 30 vigorous strokes of the piston emulsifier - described below - are usually prescribed) this method is believed to have good accuracy for routine work. It is rather difficult to obtain two extractions that will agree perfectly but it is even more difficult to attempt to isolate all the salts present in a given sample. The heavier the material, the more pronounced this difficulty becomes.

The emulsifier used for these extractions consisted of a 1 3/4 inch brass tube of sufficient length to hold about 800 ml, with a piston made of a brass disc 1/16 inch smaller than the inside diameter of the tube, and a steel rod to work the piston up and down. The bottom end was closed with a flat piece of steel and the top with a threaded cover equipped with a packing gland. A 1/8 inch brass cock was installed near the bottom of the cylinder to draw off the water extract. The entire assembly resembled a tire pump.

The procedure for making an extraction was to pipette 200 ml of oil into the brass cylinder, add 100 ml of benzene to dilute the sample and stir gently by a few strokes of the piston, then add 171 ml of very hot distilled water followed by 25 ml of acetone, which acts as an emulsion breaker. Quickly close the cylinder and emulsify the contents by 30 strokes of the piston. Allow to settle for a few minutes and withdraw into a separatory funnel. From the funnel withdraw 100 ml of the water - acetone mixture, through a qualitative filter paper to remove all traces of oil, for titration. For the titration a Leeds and Northrup Potentiometer-pH Meter was used. The titration cell consisted of a standard calomel cell versus a silver-button electrode. The 100 ml of chloride solution was carefully evaporated to 5 to 10 ml and rediluted with 95 ml of anhydrous denatured alcohol and titrated with .05 N silver nitrate. An air-driven stirring motor was used to agitate the solution and the results were plotted in the usual manner for potentiometric titrations; ml of titrating reagent versus e.m.f. of the cell.

In connection with these chloride titrations the writer employed a special titrating medium which is not commonly employed or it may have never been employed for this purpose. The medium used was Solox which is a commercial alcohol sold by the U. S. Industrial Chemicals Corp, New York 17, N. Y. It is a denatured alcohol having the following approximate composition: ethyl alcohol 90%, methyl alcohol 4%, ethyl

acetate 5%, aviation gasoline 1%.

The purpose of using an alcohol for a titrating medium was to obtain a much greater inflection of the galvanometer at the end point. It is known that in dilute chloride solutions the galvanometer inflection of this cell is quite low and therefore subject to considerable error. Dr. R. W. Stensel of the Petroleum Rectifying Company, Los³² Angeles, California, has the following comment on chloride titrations: "When the chloride concentration in the extract is low, so that only .2 to .5 ml of the silver nitrate solution is required for titration, inflections are likely to ill-defined". It was discovered by the writer that this difficulty could be overcome by concentrating the dilute chloride solution to about 5 ml., adding 95 ml of alcohol and then proceeding with the titration in the usual manner. It will be observed from inspection of the titration graphs that inflection potentials are excellent and accuracy of the method is improved. A graph is included showing the types of inflection obtained for both water and alcohol media.(Fig. 11)

In regard to the special titrating solvent used, the writer has received the following comment from Dr. Stensel:³³

"We were very much interested in your letter of February 10th giving results on the titration of chlorides by your specially developed method. There is no doubt that the sensitivity of the chloride determination can be greatly increased by your procedure, and it should therefore be especially suitable for the accurate determination of low chloride concentrations. I believe that if you developed this procedure more fully it could well become the subject of a paper for the chemical journals."

REPRODUCED FROM N. S. NO. 35411
10 X 10 to two half inch, 3rd time, acetone.
Engraving, 7 X 10 16.
MADE IN U. S. A.

Fig. 471

All extractions for the purpose of making chloride determinations alone were made with the piston emulsifier. In the case of determining sulfates, iron, calcium and magnesium the piston emulsifier was far too small to permit the work to be done with any rapidity - that is, it was too small to extract a large sample (12 liters). For this purpose it was decided to use a large constant-temperature bath which would hold about five gallons. It was equipped with an electric motor which gave vigorous agitation and a coil of brass tubing in the bottom permitted the passage of steam through the emulsion to give the required temperature for making successful extractions.

After making a trial extraction it was found that this apparatus would give an efficient extraction by using two portions of water. The procedure was to agitate the oil, benzene, and water for a period ranging up to 30 minutes (time of agitation is limited by the tendency of the sample to form stable emulsions) with the temperature of the entire mixture raised to 140° F. (This was considered as high as the temperature ought to be raised for safety). Near the end of the stirring period the acetone was poured in cautiously and allowed to stir for a short time. This seemed to start the emulsion to breaking. The entire mixture was

allowed to settle for 12 to 24 hours and the water-acetone layer siphoned off. An additional quantity of water was then added to the agitator and stirred vigorously for five minutes and more acetone added. After settling for 12 to 24 hours the second extract was withdrawn and added to the first. It was found that this gave a high percentage removal of the salts present. The exact quantities of sample and extractants will appear below with the extraction to which they apply.

The entire extract from a given sample was concentrated by boiling. It was necessary to add concentrated HCl to these extracts to prevent iron from adhering to the sides of the evaporation beakers during the evaporation. Ten ml. of acid was sufficient to hold the iron in solution and as these large extracts were not to be analyzed for chlorides, the addition of HCl was not considered objectionable. The extract from each sample was concentrated to exactly 1 liter. This was done in order to take aliquot portions for analyses and a relation between the sample extracted and the quantity of extract analyzed had to be known in order to compute results.

DETERMINATION OF SULFATE²

The determination of SO_4 was very simple. 100 ml of the 1 liter extract was pipetted into a beaker, heated to boiling and 20 ml of 10% Barium chloride solution added dropwise with constant stirring. After 24 hour digesting time the Barium sulfate was filtered on to a Whatman 42 filter, washed free of chloride ions, dried and ignited at $800^{\circ}C$. in a muffle furnace, cooled and weighed as Barium sulfate.

DETERMINATION OF SAMPLE WEIGHT

In order to determine the weight of all salts present in the 1 liter extract, 50 ml of the extract was evaporated to dryness on the steam bath, in a tared porcelain crucible. The crucible was then heated to constant weight in a muffle furnace at $450^{\circ}C$. In arriving at the weight of the salts in these evaporations, considerable difficulty was experienced. The extracts contained quantities of organic material dissolved in the water-acetone mixture. This could not be

oxidized easily without danger of changing the nature of the salts in the sample, so the most logical method of disposing of the organic matter was ignition. It was found that if the ignition was run at 100° C. most of the organic matter remained; at 450° C. reasonably constant weights could be obtained, but if the temperature was raised to 600 to 650° C. the samples lost considerable weight, and the losses continued in milligram amounts each time the heating was repeated for 2 hours. It was therefore concluded that the salts were slightly volatile or that some unknown change in their composition was taking place at the higher temperatures.

DETERMINATION OF IRON⁵

Take 250 ml of the 1 liter concentrated extract, add bromine water until a distinct change of color is seen, indicating an excess; then boil and add 6N ammonia until its odor just persists after blowing away the vapor. Heat to boiling again and filter as soon as the iron flocculates. Filter at once through a rapid quantitative paper, wash free of chloride, ignite at 800° C., and weigh as Fe_2O_3 .

DETERMINATION OF CALCIUM⁶

The filtrate from above is ready for processing for Calcium. Make it barely acid to litmus if it is to be left for any length of time. Add to the solution 3 drops of methyl red indicator and bring carefully to the end-point tint with 6N HCl or NH_4OH , as the case requires. Be exact about this, and when the solution is properly neutralized add 2 cc. excess acid. Heat the solution now to boiling and add with stirring half of a solution containing 1.5 gm. of ammonia oxalate. Proceed then to neutralize with 3N ammonia (1 part concentrated to 4 parts of water) until a precipitate begins to form. Continue to add the ammonia, still more slowly, until the methyl red just turns a permanent yellow (pH 6), and then add nearly all the remaining oxalate solution. Finally add 2 cc. of the 3N ammonia in excess, warm on the steam bath for half an hour, and then let stand to cool for another hour. During this cooling the precipitation is completed and the precipitate becomes more granular. When the precipitate has settled add a few drops more of the oxalate solution to see that precipitation is complete, adding more oxalate, of course, if it proves not to be. Reserve a small amount of the oxalate to be

used later. Filter as usual, washing the precipitate only twice with cold water, and taking no particular care to remove the last traces of precipitate from the beaker. Reserve this filtrate for magnesium.

Place the original beaker under the filter and proceed to dissolve the calcium oxalate by pouring over it hot 3N HCl. This should be added drop by drop so as to allow time for solution. When it is all in solution wash the filter, first with water, and finally with a few drops of ammonia to remove the acid. Dilute the filtrate to 100 cc., and add 3 drops methyl red, heat to boiling, and then slowly neutralize with ammonia until the methyl red just turns yellow. In this way the calcium oxalate is reprecipitated. To make this precipitation more complete the remainder of the ammonium oxalate is now added (common ion effect). After 15 minutes or longer filter through the original paper, adding this filtrate to the one already reserved for magnesium. If this solution is to be left for any great length of time it is well to have it faintly acid to prevent action on the glass.

Remove the filter and contents from the funnel, taking care not to neglect any solid particles which may be on the glass, and place in a weighed crucible. Dry, and finally ignite, gently at first until the paper is all consumed, and finally more strongly, with crucible inclined, until the precipitate is white. The calcium is then partly in the condition of mostly carbonate and partly oxide.

From here on, two methods of procedure are possible: One is to ignite at a very high temperature (about 1000° C.) until the carbonate is completely changed to oxide; and the other is to transform the whole into sulfate by ignition with ammonium sulfate. Considering our usual inability to get such a high temperature, particularly in porcelain crucibles, we shall use the latter method, as follows:

After ignition has been carried as far as possible with a Bunsen flame, let the crucible cool until it can be held in the hand, and then add 1 gm. of pure ammonium sulfate which leaves no residue on ignition, cover the crucible and heat gently (in a hood) until the excess of ammonium sulfate is expelled. Finally raise the temperature moderately for a short time to make sure that none of the ammonium salt remains on the walls of the crucible, cool in a desiccator, and weigh as CaSO_4 .

DETERMINATION OF MAGNESIUM⁵

The combined filtrates from calcium now have a volume of probably 300 or 400 cc. This is too large for accurate precipitation of magnesium, since the double phosphate is rather soluble. Place this solution in a beaker and proceed to evaporate it down to smaller volume on a steam bath. (It should not be boiled because of the danger of spattering.) The solution was faintly acid during this evaporation. Evaporate to the point where the salts present begin to crystallize out, and then add just enough cold water to bring them all back into solution. The solution should be perfectly clear; if it is not, it should be filtered. The volume should not exceed 100 cc. To this solution add 2 drops of methyl red indicator, and then drop in just enough 3N ammonia to turn the indicator yellow.

Prepare a solution of diammonium hydrogen phosphate, $(\text{NH}_4)_2\text{HPO}_4$, containing 2 gm. of the solid 10 cc. water. Add this dropwise to the above solution, stirring constantly. Finally add concentrated ammonia until the amount is $1/6$ that of the original solution (perhaps 20 cc.). Stir vigorously for 10 minutes, and then allow the mixture to stand for six hours, or preferably, over night.

Filter off the precipitate and wash it with 2.5 per cent ammonia (1 part concentrated to 10 of water), then redissolve by proper use of 10 cc. 3N HCl, as with the calcium receiving the solution in the precipitation beaker and washing the paper thoroughly. Proceed then to reprecipitate by first adding a solution containing about 0.1 gm. of the diammonium phosphate, and then slowly neutralising with dilute ammonia to the methyl red end-point. Finally add again 1/6 volume of concentrated ammonia with thorough stirring, and allow to stand for six hours or over night.

The precipitate this time should be pure $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. Filter on the original paper, washing with 2.5 per cent ammonia (1 : 10) until a sample of the wash water acidified with nitric acid gives no more than a faint opalescence with silver nitrate--that is, until chlorides are removed.

Place the paper and precipitate in a porcelain crucible and dry completely without charring, and then increase the heat very gradually until the paper is consumed and the precipitate is white. Cool and weigh as $\text{Mg}_2\text{P}_2\text{O}_7$.

METHOD FOR DETERMINATION OF AMMONIA AND CHLORIDE IN SALTS ^{38, 28}

In the salt isolated from the cracked gasoline condenser it was found that the NH_4 and Cl^- ions were present. In the analysis for chloride the Mohr Method was used. (The potentiometer was not available at this time.)

Mohr Method for Chloride ³⁸

A sample of the salt was isolated from the wash water coming from the condenser. The salt was dried at 100°C. and a .3 gram

sample weighed from a weighing bottle into a casserole, dissolved in 100 ml of distilled water, 5 ml of 5% K_2CrO_4 indicator added and then titrated to the first red color with .1 N. $AgNO_3$. From the volume used the percentage of chloride was calculated.

Method for Determination of NH_3 ²⁸

A sample of above salt weighing .4 gram was carefully placed in a 100 ml distilling flask and carefully dissolved in distilled water. 100 ml of .1 N. HCl was measured into a beaker and placed under the adapter at the end of a Leibig condenser. An excess of strong $NaOH$ was quickly added to the distilling flask and the thermometer quickly inserted (without any agitation of the flask) and a distillation of the NH_3 begun into the excess of standard HCl . Upon completion of the distillation, the condenser was rinsed down and the excess HCl back-titrated with .1 N. $NaOH$. From the amount of HCl neutralized by the NH_3 the percent of NH_3 in the sample was calculated.

METHOD FOR DETERMINING QUANTITY OF ACID PRODUCED BY DISTILLATION³⁵

The quantity of acid produced by distillation can be estimated in the laboratory as follows: Charge 500 ml of the crude oil into a 1000 ml side-neck flask fitted with a steam connection. Connect the flask to a condenser and the condenser to an Erlenmeyer flask. Connect the vent from the flask to an ASTM sulphur determination absorber (D 90-34F). The absorber is charged with 45 ml of 1/16 N sodium carbonate solution (5.306 grams per liter).

The oil is heated and steam is applied at an oil temperature of $240^{\circ}F$. The distillation is continued at a rate so as to reach an oil temperature of $650^{\circ}F$. in 1 hour. Sufficient steam is used to give

about 40 ml of water condensate overhead. The overhead is water-washed twice in a separatory funnel and the wash water added to the absorber. The solution in the absorber is back-titrated with standard hydrochloric acid (.08625N) using methyl orange as an indicator. (ml. acid for blank - ml. acid for titration) X 2.2 = lbs. hydrochloric acid per 1000 barrels of oil. This laboratory method makes it possible to compare the acid products which might be obtained from the various crudes processed at a plant before and after desalting operation.

ANALYTICAL DATA

Since each refining process has its own characteristics which make it different from other processes; the distribution of salts in the Astma process is probably slightly different from other processes. In studying these salts the principal things to determine were:

1. What principal salts were present in the crude oil.
2. How much of each.

Similar data on the salts present in the topped crude (all straight-run distillates removed) and residual fuel oil would also be of interest. The salts present in deposits taken from points of fouling would also have some significance. Before beginning any systematic study of the salts, certain known generalities were considered. In routine laboratory testing for salts it is customary to use the chloride ion as an index to the total quantity of salts present. To make this index worthwhile it is necessary to know the relationship between the quantities of chloride, sulfate, iron, sodium, calcium and magnesium. The quantities of chloride ion present in crude oils normally processed at Astma Oil Company were known but no information was available on the relationship between chloride and other ions. It was known that Astma crude oils contained from 10 to 40 grams of chloride as sodium chloride per barrel of crude oil. The crude oil at the time the study started, contained 20 to 30 grams per barrel of sodium chloride. (1 gram per bbl. of 42 gal. is equal to 2.2 pounds per 1000 bbls.)

From this fact, it was obvious that a sizeable quantity of crude oil would have to be extracted in order to have enough for analysis. It was also obvious that some method other than usual laboratory procedure would be required if this extraction was to be performed with any ease and speed. After trying a number of methods it was decided to use the method of Petroleum Rectifying Company, Los Angeles, Calif.³¹

(with modifications) for the determination of chlorides, a general method for sulfates, and the methods of Chapin⁴ for iron, calcium and magnesium. For all samples except chloride a special extractor was used which would hold five gallons in order to extract sufficient sample in a single batch. (See Analytical Methods).

The experimental work presented represents 75 to 100 tests and experiments of various types. Quantitative work was run in duplicate.

Table I

Qualitative Analyses for Ions in extracts from crude oil:

1. Chloride	Present
2. Sulfate	Present
3. Iron	Present
4. Calcium	Present
5. Magnesium	Present
6. Sodium	Present
7. Organic Matter	Present

Quantitative analyses were run for each ion and tabulations of findings follow. Sodium and organic matter were calculated as one component by deducting the sum of the first five ions from 100. Results were calculated in terms of pounds of NaCl or Na_2SO_4 per thousand barrels (ptb) of oil and in terms of percents by weight of each ion in the total weight of salts. The ptb method of expressing results is more widely used than percentage composition and ptb results are more trustworthy for reasons to be explained later.

ANALYSES OF SAMPLES FOR CHLORIDE CONTENT

In order to determine the chloride content of the samples, and the efficiency of the batch extractor, the oils were analysed for chloride ions before and after extraction with the batch extractor. The procedure is described under analytical methods and titration graphs are given on next three pages. In all cases 1 ml of .05 N AgNO_3 is equal to 10 pounds of NaCl per 1000 barrels (1 bbl. = 42 gal.) of oil. It was noted that in each case the batch extractor reduced the chloride content to approximately 2 ptb. (Figs. 12, 13, 14)

Extractions were made as follows:

Crude Oil	12 liters
Topped Crude	8 liters
Residual Fuel Oil	4 liters

In each case the total extract was concentrated, by boiling, to exactly one liter. Analyses for iron, calcium and magnesium were made by taking 250 ml aliquot portions of this liter extract and processing it as described under analytical methods. A 100 ml aliquot was used for the sulfate analysis. Chloride analyses were not concerned with the liter extract but were made as described under analytical methods.

Fig. 12

KEUFFEL & ESSER CO., N. Y. NO. 250-11
10 X 10 to the half inch, 5 1/2 lines across
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Table II

DETERMINATION OF WEIGHT OF SALTS IN LITER EXTRACTS

	Crude Oil	Topped Crude	Residual Fuel Oil
Ml. of oil represented by 50 ml aliquot of liter concentrate	600	400	200
Wt. of salts upon evap. of 50 ml of liter concentrate, dried at 100° C.	.2083 g	.1048 g	.0703 g
Wt. of salts per ml of liter concentrate (using 100° C wts)	.004166 g	.002092 g	.001406 g
Wt. of salts upon heating above to 450° C.	.1183 g	.0838 g	.0638 g
Wt. of salts per ml of liter concentrate (using 450° C wts)	.002366 g	.001670 g	.001276 g
Wt. of salts upon heating above to 600° C.			
1 heating of 2 hrs.	.1148 g	.0777 g	.0568 g
2 heatings of 2 hr. ea.	.1139 g	.0771 g	.0546 g

It will be noted that each sample lost weight each time the temperature was increased. The loss between 100° C and 450° C was due mostly to loss of organic matter. The losses between 450° C and 600° C and at 600° C are due to unknown causes, presumably changes in the salts are taking place. Relatively constant weights were obtained at 450° C so these weights are probably the most trustworthy of the group.

It is apparent that obtaining a highly accurate sample weight, upon which to base percentage figures, would be difficult due to interference of organic matter.

Table III

**EFFECT OF TEMPERATURE UPON SALTS
(Calculated from Table II)**

Using wts. @ 100°C			
	Crude Oil	Topped Crude	Residual Fuel Oil
Percent of crude oil	100	89	33.3
Wt. of salts per 100 ml, actual	.0347 g	.0262 g	.0352
Wt. of salts found, based on crude oil	.0347	.0154	.0117
Percent of salts found	100	44.4	33.8
Percent of salts lost		55.6	66.2
Using wts. @ 450° C			
Wt. of salts per 100 ml, actual	.0197	.0209	.0319
Wt. of salts found, based on crude oil	.0197	.0123	.0106
Percent of salts found	100	62.5	53.8
Percent of salts lost		37.5	46.2

It will be observed that the loss at 100° C. was 18% greater than at 450° C. on passing from crude to topped crude. On passing from topped crude to residual fuel oil (by cracking distillation) the loss is only two percent greater at 100° C. than at 450° C. This 20% difference was due largely to organic matter which was mostly destroyed when the temperature was raised to 450° C.

It is apparent, therefore, that most of the organic matter will be destroyed or deposited in topping distillation. It is also apparent that 4 or 5 times as much salt is lost in topping distillation as in cracking distillation and consequently difficulties in topping stills will be much greater due to salts than in cracking stills.

Table IV

DETERMINATION OF FREE HCl FORMED BY STEAM DISTILLATION OF CRUDE OIL

	Sample Number	
	I	II
Size sample used, ml.	500	500
Distill as per analytical procedure		
Omit absorber for H ₂ S and boil distillate to expel any H ₂ S collected		
ml NaOH required, .08623 N	2.41	2.48
ml NaOH .08623 N X 2.2 = ptb of HCl	5.30	5.45
Average, ptb HCl formed	5.38	

From Table V it is shown that crude oil contained 46.8 ptb of NaCl. As considerable steam is used in topping distillation it is possible for 11.5% of the total chloride content to become free HCl, which would be very corrosive in towers and condensers.

Table V

SALTS FOUND IN CRUDE OIL, TOPPED CRUDE AND RESIDUAL FUEL OIL

	<u>Material Analyzed</u>		Residual Fuel Oil
	Crude Oil	Topped Crude	
Gravity, °API/sp.gr.	35.5/.8473	24.0/.9100	16.0/.9593
Percent of crude oil	100	59	33.3
Percent of topped crude		100	56.5
Chloride content, as NaCl, pth	46.8	65.3	101.3
Sulfate content, as Na ₂ SO ₄ , pth	29.0	33.2	33.9
Iron content, as NaCl, pth	6.27	3.33	1.38
Calcium content, as NaCl, pth	20.7	20.5	19.4
Magnesium content, as NaCl, pth	<u>4.08</u>	<u>3.75†</u>	<u>7.45</u>
Total	106.85	126.08	163.43
*Total extractable solids, pth heated to 100° C.	121.5	91.5	123.0
*Total extractable solids, pth heated to 450° C.	69.0	73.1	111.7
**Percent lost on raising temp. from 100° C. to 450° C.	43.3	20.1	9.2

* Weights not used in computing above data.

** Includes organic matter.

If the chloride ion is used as an index of the quantity of salts present, the chlorides represent 60% and sulfates represent 40% of the total.

The magnesium content of the salts in topped crude is believed to be in error as evidenced by later computations.

Table VI

TOTAL EFFECT OF BOTH TOPPING AND CRACKING DISTILLATION UPON SALTS

(calculated from Table V)

	<u>Actual ptb in Crude</u>	<u>Calc. ptb in Resid.F.O. if no loss occurred</u>	<u>Actual ptb found in Resid.F.O.</u>	<u>% found</u>	<u>% lost</u>
Chloride, as NaCl	46.8	140.4	101.3	72.1	27.9
Sulfate, as Na ₂ SO ₄	29.0	87.0	33.9	39.0	61.0
Iron, as NaCl	6.27	18.81	1.38	7.34	92.7
Calcium, as NaCl	20.7	62.0	19.4	31.2	28.8
Magnesium, as NaCl	4.08	12.24	7.45	60.8	39.2
Total extractable solids:					
*heated to 100° C.	121.50	364.5	123.0	33.8	66.2
heated to 450° C.	69.00	207.0	111.7	53.8	46.2

* Includes organic matter.

Approximately half of total salts are lost.

The sulfate loss is approximately twice as great as the chloride loss.

Losses of metallic ions vary from 40 to 90 percent.

It is reasonable to assume that some of the ions lost combine with the oils and remain oil-soluble compounds. Any such compounds probably cause no difficulties in the fouling and corrosion category.

Table VII

INDIVIDUAL EFFECTS OF TOPPING AND CRACKING UPON SALTS
(calculated from Tables V & VI)

	Actual ptb. in crude oil	Calc. ptb. in topped crude if no loss	Actual ptb. in topped crude	% found	% lost in topping	% lost in both topping and cracking (Table VI)	% lost in cracking (by dif.)
Chloride, as NaCl	46.8	79.4	65.3	82.3	17.7	27.9	10.2
Sulfate, as Na ₂ SO ₄	29.0	49.2	33.2	67.5	32.5	61.0	28.5
Iron, as NaCl	6.27	10.6	3.33	31.4	68.6	92.7	24.1
Calcium, as NaCl	20.7	35.1	20.5	58.4	41.6	68.8	27.2
Magnesium, as NaCl	4.08	6.91	3.75†	54.3	45.7†	39.2	-----
Total extractable solids:							
*heated to 100°C	121.50	205	91.5	44.6	55.4	66.2	10.8
heated to 450°C	69.0	117	73.1	62.5	37.5	46.2	8.7

* Includes organic matter.

Losses of chlorides in topping distillation is approximately twice as great as cracking distillation. Sulfates show about equal losses in each operation.

In general, losses are 4 to 5 times as great in topping distillation as in cracking distillation. This agrees with a generally accepted fact that the principal difficulties due to salts are experienced in topping stills.

Table VIII

PERCENTAGE COMPOSITION OF SALTS

	<u>Material Analyzed</u>					
	Crude Oil		Topped Crude		Residual Fuel Oil	
Gravity, °API/Sp.Gr.	35.5/.8473		24.0/.9100		16.0/.9593	
Percent of crude oil	100		59		33.3	
Percent of topped crude			100		56.5	
Temp. to which sample was heated, °C.	100	450	100	450	100	450
Chloride, as Cl, %	23.50	41.30	43.70	54.50	50.30	55.70
Sulfate, as SO ₄ , %	16.10	28.35	24.60	30.75	18.60	20.50
Iron, as Fe, %	2.48	4.36	1.74	2.17	.54	.59
Calcium, as Ca, %	5.58	9.86	7.28	9.12	5.16	5.69
Magnesium, as Mg, %	.69	1.21	.84	1.05	1.24	1.37
*Sodium, (by diff.), %	<u>51.65</u>	<u>14.92</u>	<u>21.84</u>	<u>2.41</u>	<u>24.16</u>	<u>16.15</u>
Total	100.00	100.00	100.00	100.00	100.00	100.00

* Includes organic matter.

The wide variance of the percentage figures may be attributed to loss of organic matter (or other unknown changes) when the temperature was raised on the sample. From Table II it will be noted that organic matter was estimated at approximately 20% of the sample weight. Interference of organic matter can be alleviated by taking a brine sample from the bottom of a storage tank and processing it for various ions, but such procedure was not practicable in this study as it was desired to learn what effects the Astma Refining Process had on salts.

Since accurate percentage weights are difficult to obtain, it is accepted analytical practice to compute results in terms of pounds per 1000 barrels of oil. This, being a weight to volume ratio, is not

Table VIII (Cont'd)

affected by unknown factors such as organic matter and water of hydration. It is probable that salts from a given crude oil vary over limited ranges in percentage composition and for practical purposes highly precise percentage analyses are not justified.

Table IX

POUNDS PER 1000 BARRELS (ptb) OF IONS IN SALTS
(calculated from Table VIII)

	<u>Material Analyzed</u>				<u>Residual</u>	
	Crude Oil		Topped Crude		Fuel Oil	
Gravity, °API/sp.gr.	35.5/.8473		24.0/.9100		16.0/.9593	
Percent of crude oil	100		59		33.3	
Percent of topped crude			100		56.5	
Temperature to which sample was heated, ° C.	100	450	100	450	100	450
Chloride, as Cl, ptb	28.55	28.55	39.99	39.99	62.00	62.00
Sulfate, as SO ₄ , ptb	19.56	19.56	22.50	22.50	22.87	22.87
Iron, as Fe, ptb	3.01	3.01	1.59	1.59	.66	.66
Calcium, as Ca, ptb	6.78	6.78	6.66	6.66	6.35	6.35
Magnesium, as Mg, ptb	.84	.84	.77†	.77†	1.53	1.53
*Sodium, by difference, ptb	62.76	10.26	19.99	1.59	29.59	18.29
Total extractable solids, ptb	121.50	69.00	91.50	73.10	123.00	111.70

* Includes organic matter.

It will be observed that the pounds per 1000 barrels of oil of all ions, except sodium, are identical, even though the temperatures are different. This illustrates the desirability of using weight to volume relationship instead of weight percent relationship for expressing results. It is shown that on the ptb relationship chlorides increase progressively as distillates are removed while sulfates remain constant. This suggests greater stability both chemically and physically for the chlorides over the sulfates.

It is also shown that iron is largely lost, calcium remains constant and magnesium increases. Magnesium salts are considered the most

Table IX (continued)

dangerous due to hydrolysis, but in this study they may be ignored due to small quantity present.

Table X

TOTAL EFFECT OF TOPPING AND CRACKING DISTILLATION UPON IONS
(computed from Table IX)

	Ptb in crude oil	ptb in residual fuel oil if no loss occurred	ptb found in residual fuel oil	% found	% lost
Chloride	28.55	85.65	62.00	72.39	27.61
Sulfate	19.56	58.68	22.87	38.97	61.03
Iron	3.01	9.03	.66	7.31	92.69
Calcium	6.78	20.34	6.35	31.22	68.78
Magnesium	.84	2.52	1.53	60.71	39.29
*Sodium, at 100° C.	62.76	186.28	29.59	15.72	84.28
Sodium, at 450° C.	10.26	30.78	18.29	59.42	40.58
Total, at 100° C.	121.50	364.50	123.00	33.74	66.26
Total, at 450° C.	69.00	207.00	111.70	53.96	46.04

* Includes organic matter.

It will be observed that these losses agree closely with those shown in Table VI. This was expected as the same basic data are involved. In this table, only the weight of the ion determined is shown, whereas Table VI is based on hypothetical combinations of ions.

Table XI

Analysis of salt isolated from wash water taken from cracked gasoline condenser. This salt was proved to contain NH_4 and Cl ions.

Analysis for Chloride by Mohr Method

Wt. salt taken for analysis	0.3382
Ml. AgNO_3 (.1000N) for titration	61.40
Percent chloride in sample	64.37
Percent chloride in pure NH_4Cl	66.27
Percent NH_4Cl in sample	97.13

Analysis for NH_3

Wt. salt taken for analysis	0.4147
Ml. of HCl (0.1000N) for titration	74.80
Percent NH_3 in sample	30.66
Percent NH_3 in pure NH_4Cl	31.78
Percent NH_4Cl in sample	96.49

It is therefore shown that this salt was predominantly NH_4Cl . The chloride (or HCl) ion doubtless was produced from the salts present in the oil, while the NH_3 was introduced as a gas into the system to combine with the free hydrochloric acid.

Table XII

RESULTS OF DESALTING WITH PETRECO DESALTERS

AT AETNA OIL COMPANY, LOUISVILLE, KENTUCKY

During the past year the desalters at Aetna Oil Company have produced salt removal as follows: Results are based on analyses of crude oil for chloride ion before and after desalting.

	ptb NaCl in crude oil	ptb NaCl in desalted crude	% NaCl removal
1946			
April	35.4	3.9	89
May	28.5	1.6	94
June	23.1	3.3	86
July	23.0	4.7	80
August	16.6	3.9	77
September	20.6	4.0	81
October	22.0	5.1	77
November	23.8	5.0	79
December	34.1	5.0	85
1947			
January	33.3	4.3	87
February	55.6	6.4	88
March	46.2	6.0	87
Average			84

In view of the reasonably low salt content of the desalted crude oil it may be assumed that corrosion in the refinery system due to HCl was very low. Plugging of heat exchangers with salt has been negligible. Deposition of ammonium chloride in the cracked gasoline condenser has been very low. It is believed that practically all troubles due to salts have been removed.

CONCLUSIONS

CONCLUSIONS

1. Losses of crude oil salts in petroleum refining approximate fifty percent.
2. Losses of chlorides are only half as great as sulfates.
3. Four times as much salts are lost in topping distillation as in cracking distillation. Therefore, much greater difficulties due to fouling and corrosion (caused by salts) may be expected in topping stills as compared with cracking stills.
4. An alcoholic medium is superior to an aqueous medium when determining chloride ion concentration potentiometrically.
5. The chloride ion, when used as an index, is equal to 60% of the salts present.
6. Installation of desalters at Aetna Oil Company removed an average of 84 percent of the salts present in crude oils.

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