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Source Control and Treatment of Contaminants Found in Petroleum Product Terminal Tank Bottoms



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Source Control and Treatment of Contaminant Found in Petroleum Product Tank Bottoms

**Health and Environmental Sciences and
Manufacturing, Distribution and Marketing
Departments**

API PUBLICATION NUMBER 4606

PREPARED UNDER CONTRACT BY:
W.T. WANG, J. GUMULKA, AND P.T. SUN
SHELL DEVELOPMENT COMPANY
ENVIRONMENTAL R, D, & T DIRECTORATE
HOUSTON, TEXAS

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API STAFF CONTACT

Priscilla J. Young, Manufacturing, Distribution & Marketing Department

MEMBERS OF THE MARKETING TERMINAL EFFLUENT TASK FORCE

Robert R. Goodrich, *Chairman*, Exxon Research and Engineering Company

Dave Pierce, *Vice-Chairman*, Chevron Research and Technology

Jeff Baker, Conoco Inc.

Terrie Blackburn, Williams Pipeline

Sanjay Dhawan, Amoco Oil Co.

Don Hitchcock, Texaco Refining and Marketing

Nancy Kralik, Marathon Oil Co.

LeAnne Kunce, BP Oil

Al Schoen, Mobil Research & Development

Marilyn Shup, Sun Refining and Marketing

Paul Sun, Shell Development Co.

Carl Venzke, Citgo Petroleum

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PREFACE

This report presents the results of one of a series of technical studies sponsored by the American Petroleum Institute (API) to characterize petroleum product terminal wastewaters and to identify sound technology for handling and treating them. The results of this research program are intended to provide industry and regulatory agencies with sound technical information needed to make informed decisions on appropriate technology that can be considered for individual facilities.

Prior work has shown that the wastewaters generated at petroleum product terminals vary greatly in their quality and types of contamination. This study focused on those small amounts of waters generated in petroleum product tanks at terminals since these waters are removed at different frequencies to ensure product quality (minimize water contamination). The prior studies showed that some terminal tank bottom waters contain elevated concentrations of ammonia and metals. These compounds would be difficult to remove at the terminal. Many terminals currently take these waters directly from the tanks and send them back to refineries or industrial facilities that can recover the product from the water/product mixture. The main activity in this present study (Phase I), conducted by Shell Development Company, was to identify the sources of the metal or ammonia contamination and potential options to prevent them from entering terminal waters. In Phase II the performance of two treatment technologies that have potential for use at terminals was evaluated.

The results of the study showed that some potential source control options or operating changes could be done at the refinery to reduce the presence of these contaminants in terminal tank bottom waters. The alternative is to add wastewater treatment facility modifications at the terminal, which may be expensive both in hardware and additional staffing. The Phase II work evaluated combinations of biological treatment (activated sludge), activated carbon and a magnesium/aluminum oxide sorbent and showed that removal of metals, particularly arsenic, was much more challenging than expected. The overall conclusion of this study was **"removal of metals and ammonia either at the refinery or with treatment equipment at the distribution terminal was found to be more difficult than expected."** Hence, it is recommended that terminal operators and engineers carefully evaluate tank bottom water treatment/recycling options for individual terminals. In most cases, it appears that these product/water mixtures can be handled best by returning them to refineries or firms that can recover the product, thus minimizing environmental impact and water treatment costs.

The API, through its Marketing Terminal Effluent Task Force, acknowledges and appreciates the excellent efforts of Shell Development Company staff in conducting this research. The activities reflect a multi-disciplined team working on a complicated set of technology problems, everything from the use of sophisticated analytical methods for arsenic speciation to the use of very experienced and specialized expertise in petroleum industry wastewater treatment technology. The Task Force thanks the Shell Development team for their extra efforts on this project.

R.R. Goodrich
ON BEHALF OF THE MARKETING
TERMINAL EFFLUENT TASK FORCE

ABSTRACT

Tank bottoms generated at petroleum product distribution terminals may contain dissolved organics, ammonia, and trace heavy metals. Previous studies have shown that elevated levels of ammonia, arsenic, copper and zinc in some tank bottoms samples may be toxic to fish. This project investigated the sources of these substances in tank bottoms and identified potential source control methods. The feasibility of two treatment systems used to remove organics and metals was also evaluated. The source identification study included sampling, analysis and speciation of the metal compounds of interest in tank bottoms as well as various process streams in a refinery. The treatment technologies were evaluated using laboratory scale units. The study showed that compounds of arsenic, copper and zinc are highly soluble in aqueous solutions and could migrate to tank bottoms via two pathways. The data on the fate of copper and zinc appeared to be erratic, suggesting that cross contamination might contribute to the copper and zinc found in tank bottoms. Potential sources of contamination included corrosion of process equipment and leaching of the coating primer used for storage tank protection. The crude oil processed at the refinery contained very little selenium; consequently, the fate of selenium could not be studied. Ammonia and organic nitrogen compounds were widely found in the tank bottoms of various refined products and in spent caustic solutions. There is circumstantial evidence that organic nitrogen compounds in tank bottoms were slowly transformed to ammonia through unknown chemical reactions. Since the compounds of arsenic, copper, zinc, organic nitrogen and ammonia are very soluble in water, additional steps of product washing and improved separation of washing solutions from products at the refinery are two potential source control solutions. The results of the laboratory treatment studies showed effective removal of organics, copper, and zinc, but not arsenic. Additional source control in refineries appears to be the best potential solution to effectively prevent heavy metals and ammonia from getting into the tank bottoms at distribution terminals. The results of this study were from sampling/analysis at only one refinery. Therefore, data on the compositions of petroleum products and the contaminant levels in the tank bottoms are not necessarily representative of those in other refineries. Hence, caution should be exercised in applying the results to other specific products or locations.

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EXECUTIVE SUMMARY

Tank bottoms generated at petroleum product distribution terminals may contain dissolved organics, ammonia, and trace metals. Previous API sponsored studies showed that the presence of elevated levels of ammonia and heavy metals, particularly arsenic, copper and zinc, in tank bottoms might be toxic to fish. In the same studies, it was also shown that the toxic effects associated with ammonia and heavy metals could not be completely eliminated by biological treatment technologies such as use of a sequencing batch reactor or a rotating biological contactor. Additional treatment processes including air stripping at high pH, carbon adsorption and iron coprecipitation were necessary to achieve complete elimination of the toxic effects in most, but not all, of the tank bottoms. Such multiple treatment processes might not be easily implemented at product terminals which lack personnel and wastewater treatment capability. API's Terminal Effluent Task Force therefore sponsored this project to investigate the sources of heavy metals and ammonia found in tank bottoms and to identify potential source control methods for these metals.

This project consisted of two phases: Phase I identified the sources of ammonia, arsenic, copper, selenium and zinc found in terminal tank bottoms; and Phase II evaluated the feasibility of two tank bottom treatment technologies that could be implemented and operated in distribution terminals.

Phase I of this study involved sampling, analysis and speciation of the compounds of interest in tank bottoms, refined products and refining process streams. The results show that the arsenic compounds generated in the refining processes were highly soluble in water and caustic solutions. Hence, arsenic tended to partition preferentially to aqueous tank bottoms. Most of the refined products therefore contained very little arsenic with concentrations being near or below the 5 ppb detection limit. Among the gasoline blending components, catalytic gasoline and alkylate contained the highest arsenic concentration prior to caustic treatment and blending.

Speciation of arsenic compounds in the tank bottoms of gasoline products and gasoline blending components identified monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), arsenite, arsenate, and several organoarsenic compounds with unknown chemical structures and formulae. Only three of the unknown organoarsenic compounds were quantifiable. The arsenic species found in the tank bottoms of the gasoline products were completely accounted for by the combination of the arsenic species found in the tank bottom of alkylate and in the spent caustic

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of catalytic gasoline. Therefore, it is confirmed that catalytic gasoline and alkylate are the major sources of arsenic.

This study identified two potential pathways through which arsenic could enter the tank bottoms: (1) if the arsenic compounds in the gasoline blending components, particularly catalytic gasoline and alkylate, were effectively removed in caustic or water washing processes, arsenic could become concentrated in the aqueous wash solution. Poor separation of the wash solution from the hydrocarbon phase of the blending components could result in entrainment of the wash solution in droplet form into the final gasoline products. The entrained aqueous droplets, which contained concentrated arsenic, were eventually separated from the hydrocarbon in the storage tank and settled as the tank bottom. (2) If the water wash or caustic treatment did not effectively remove arsenic from the products, the products would contain trace arsenic concentration. Since the arsenic compounds were highly soluble in water and a large volume of product was in prolonged contact with a small quantity of tank bottoms, the arsenic compounds would partition to and become concentrated in tank bottoms.

The data on the fate of copper and zinc through the refining and the product blending processes were erratic, suggesting that in addition to being indigenous to the crude oil, copper and zinc found in tank bottoms could come from corrosion of process equipment and/or from leaching of the constituents of the coating primer (containing zinc) used for storage tank protection. In addition, the copper and zinc compounds found in tank bottoms exhibited high water solubility. Therefore, they could also enter tank bottoms through the same mechanisms described above for arsenic compounds.

Very high salt contents existed in the tank bottom samples, which significantly reduced the analytical sensitivity of selenium. In addition, very little selenium was found in the crude, refined products, and their tank bottoms. Consequently, identification of the source of selenium was not attempted.

Ammonia and other organic nitrogen compounds were widely found in the tank bottoms of various refined products and in spent caustic solutions. Since both the organic nitrogen compounds and ammonia are highly soluble in water, they can migrate from refining processes to the tank bottoms of products at distribution terminals via the same pathways identified for arsenic species. The highest ammonia concentration found in the tank bottoms of the finished product tanks at this refinery was in the range of 150 ppm, considerably lower than those of

many tank bottoms surveyed in the previous API project. The spent caustic solutions did contain higher concentrations of ammonia and particularly organic nitrogen compounds. There was circumstantial evidence of conversion of the organic nitrogen compounds in the tank with ammonia as byproduct. Therefore, the organic nitrogen compounds can be the potential ammonia source in tank bottoms.

Other potential ammonia sources in the refinery are the sour waters produced in the fractionation columns after fluid catalytic cracking (FCC) and hydrotreating processes. In this refinery, separation of sour water and catalytic gasoline at the overhead condenser of the FCC fractionation column was excellent. Therefore, contamination of ammonia to the catalytic gasoline was minimal. In addition, no products from hydrotreating processes were retrieved for direct gasoline blending at this refinery. Minimum contamination of ammonia from the catalytic cracking and hydrotreating processes might be attributing to the low ammonia concentrations in the tank bottoms of this refinery.

Phase II of this study evaluated the feasibility of two treatment systems for simultaneous removal of organics and metals in tank bottoms. The two treatment systems are activated sludge coupled with iron coprecipitation and activated sludge combined with powder activated carbon. Although organic removal in the proposed processes was satisfactory, arsenic was hardly removed (approximately 8-9% removal). Up to 80% of copper and zinc were removed by the proposed treatment systems, but the removal efficiencies were inconsistent.

The arsenic compounds in tank bottoms were removable by both activated carbon and a magnesium oxide-aluminum oxide adsorbent (Sorbplus®), with carbon being the more effective adsorbent. The removal mechanism of the oxide adsorbent was most likely charge interaction and ion exchange, while that of activated carbon was primarily via hydrophobic interaction. Therefore, the arsenic compounds in the tank bottom appeared to exhibit both hydrophilic and hydrophobic characteristics. The higher solubility of some arsenic compounds in caustic solutions also indicated they might possess acidic characteristics. This is supported by the enhanced adsorption by activated carbon at low pH. Iron coprecipitation was also shown to remove the arsenic compounds, but only at an iron dosage several orders of magnitude higher than that applied in conventional iron coprecipitation processes.

Source reduction of metal compounds from refining process streams may involve modification of

the refining processes or operating conditions, and is beyond the scope of this study. However, an extensive literature review was conducted to evaluate the processes for metal removal from hydrocarbons. Most of the processes were developed for arsenic removal. Some of the processes may be candidates for further evaluation to remove arsenic from refining process streams, thus prohibiting arsenic from getting into final gasoline products and their tank bottoms.

Two approaches identified from this study can also be used to reduce heavy metals, ammonia and recalcitrant organics migrating to the tank bottoms at product distribution terminals: (1) Additional step(s) of water washing of gasoline products can remove the target compounds from the products, and retain them in the refinery where they can be more effectively removed by the large scale treatment system. (2) After the caustic or water washing processes, effective separation of aqueous droplets from products is crucial to prevent metals from entering tank bottoms. This can be achieved by improving the operation of coalescer and water-product separator downstream of the washing process. Alternatively, if excess tanks are available, additional storage tanks for the gasoline blending components can result in additional separation of aqueous phase droplets from products. They also provide sufficient time for the target compounds to re-partition to tank bottoms and are thus retained in the refinery. The drawbacks of using the intermediate storage tank option are the high cost resulting from the additional product holdup time at the refinery and the increased load to operations.

All the data presented in this study concerning the metal and ammonia concentrations in tank bottoms are collected from one particular refinery. Therefore, the data by no means represent the characteristics of tank bottoms from other refineries or marketing terminals. However, the migration mechanisms of arsenic, copper, zinc, and ammonia from products to tank bottoms identified in this study should be independent of products and locations.

Overall, removal of metals and ammonia either at the refinery or with treatment equipment at the distribution terminal was found to be more difficult than expected.

Section 1

INTRODUCTION

Tank bottoms in petroleum product terminals contain organics, ammonia, and some heavy metals. In one API sponsored project (Vuong *et. al.*, 1993), biological treatment technologies including sequencing batch reactor and rotating biological reactor have been demonstrated to effectively remove organic pollutants in tank bottoms. However, ammonia and heavy metals such as arsenic, copper and zinc were not effectively removed, and some effluent samples after the biological treatment still exhibited toxicity to *D. Magna* and *C. Dubia*.

API subsequently sponsored another project (Klock *et. al.*, 1994) to investigate the toxicity identification and reduction associated with the biologically treated tank bottoms. Initial findings of the project showed that some trace heavy metals including arsenic, copper, zinc, and selenium and ammonia in tank bottoms were part of the causes for toxicity. Table 1-1 shows the contents of arsenic, zinc, copper and ammonia in tank bottoms sampled from different product terminals of different oil companies. Significant variations in the concentrations of metals and ammonia were observed in these samples. Some tank bottoms contained very high levels of trace metals and ammonia which were very difficult to treat. In the same project, it was also demonstrated that the toxicity associated with arsenic, copper, and zinc could be eliminated if arsenic and copper were removed to less than 200 ppb, and zinc to less than 100 ppb. The toxicity associated with ammonia could also be eliminated if its concentration in the treated tank bottoms was lower than 10 ppm. In the same project, various laboratory scale batch treatment techniques including air stripping, advanced oxidation, iron coprecipitation, and activated carbon adsorption were investigated for their effectiveness in reducing the toxicity. The results showed that additional treatment including air stripping at a very large air-to-water volume ratio and iron coprecipitation with a very high iron dosage were required to effectively remove ammonia, As, Cu, and Zn. In some biologically treated tank bottom samples, however, toxicity was not eliminated even with the combination of all the tertiary treatments. In addition, the multiple step treatment processes, namely biological treatment followed by air stripping, iron coprecipitation, etc., although demonstrated to be effective, may not be practically implementable at some product terminals which lack personnel and

wastewater treatment capability. Additional drawbacks to implementing treatment in terminals are its potential to generate air emission and hazardous wastes.

Table 1-1. Arsenic, copper, zinc, and ammonia in tank bottoms from various petroleum product distribution terminals of different oil companies (from: Klock et. al., 1994)

Sample Designation	As (ppm)	Cu (ppm)	Zn (ppm)	NH3 (ppm)
A	1.978	0.017	0.180	16
B	0.125	0.790	0.113	940
C	0.154	1.400	0.678	160
D	0.258	1.250	0.143	2800
E	0.441	0.290	0.109	900
F	1.037	0.430	0.022	560
G	0.006	0.350	0.023	2500
H	0.189	2.100	0.073	4300
I	0.195	0.980	0.195	770
J	1.130	0.610	0.366	2600
K	1.098	0.210	0.666	2570

Based on the previous series of API studies, two outstanding issues surface which need further investigation: (1) Multiple treatment processes do not necessarily eliminate the toxicity problem of some tank bottoms; and (2) Even if they can achieve total toxicity reduction for some tank bottoms, the complexity of the processes may become prohibitive to cost-effectively implement in the product terminals.

API's Terminal Effluent Task Force therefore has sponsored this project to approach the toxicity reduction issues from different perspectives. Instead of focusing solely on the development of treatment technologies for toxicity reduction at the terminal, the primary focus of this project is to identify the sources of the pollutants in tank bottoms, particularly As, Cu, Zn and ammonia, to understand how the pollutants enter the tank bottoms, and to identify techniques which reduce or eliminate the pollutants at the sources. In addition, for any treatment processes to be implementable at product terminals, they must be practical, easy to operate and maintain, and cost effective.

Therefore, the second objective of this project is to evaluate the feasibility of two simplified treatment processes, which integrates biological treatment with iron coprecipitation or powder activated carbon, to simultaneously remove organics, ammonia, and metals (particularly arsenic, copper, and zinc). This study will identify the upper limits of the contaminant levels in tank bottoms that can be practically treated to the nontoxic level using the proposed treatment processes. Such limits of the contaminant levels in tank bottoms provide guidelines for determining whether product terminal tank bottoms can be treated on site or to what extent source control is needed.

Section 2

LITERATURE REVIEW

A. Distribution of As, Cu and Zn in Petroleum Refining Processes and in Petroleum Products

1. As, Cu, and Zn in Crude Oils

Arsenic, copper, and zinc are often present in crude oils. The concentrations of these elements vary significantly depending on the origin of crude oils. Table 2-1 shows data from the literature on these three elements in different crude oils. Zinc appeared to be present in significantly higher concentrations than arsenic and copper.

Table 2-1. Contents of As, Cu, and Zn in Different Crude Oils

Crude	Arsenic (ppm)	Copper (ppm)	Zinc (ppm)	Reference
Alamein	NA	4.90	NA	Abu-Elgheit et. al. (1981)
Alberta-1	0.0024	NA	0.67	Filby and Shah (1975)
Alberta-2	0.111	NA	0.459	Hitchon et. al. (1975)
California-1	0.655	0.93	9.76	Filby (1975)
California-2	0.517	0.4	12.36	Shah et al. (1970a, b)
California-3	0.092	0.79	16.83	Shah et al. (1970a, b)
California-4	0.063	6.33	17.53	Shah et al. (1970a, b)
California-5	1.112	0.93	85.8	Shah et al. (1970a, b)
California-6	0.112	0.24	7.41	Shah et al. (1970a, b)
Libya-1	0.077	0.19	62.9	Filby and Shah (1975)
Libya-2	0.077	0.19	62.87	Shah et al. (1970a, b)
Libya-3	0.152	1.7	71.91	Shah et al. (1970a, b)
Libya-4	0.343	0.23	12.93	Shah et al. (1970a, b)
Louisiana	0.046	0.13	3.57	Shah et al. (1970a, b)
Venezuela-1	0.284	0.21	0.692	Filby (1975)
Venezuela-2	0.020	NA	NA	Bergerioux et. al. (1979)
Wyoming	0.111	2.3	6.82	Shah et al. (1970a, b)

Information concerning the speciation of metals, specifically, As, Cu, and Zn, in crude oils is not well known. According to Yen (1975), copper may be associated with complexes of tetradentate ligands, arsenic may exist in organometallic compounds, and zinc may be present as carboxylic acid salts of the polar function groups of resins (Table 2-2). This generalized information, however, does not provide clear clues to the possible fate of these elements in petroleum refining processes.

Table 2-2. Classification of metallic components in petroleum (Yen, 1975).

Classes of Metallic Components	Metals
Metalloporphyrin chelates	V, Ni
Transition metal complexes of tetradentate mixed ligands	Cu, V, Ni, Fe, Co, Cr
Organometallic compounds	As, Hg, Sb
Carboxylic acid salts of polar functional groups of resins	Zn, Mo, Ge
Colloidal minerals	NaCl, Silica

Filby (1975) performed a series of analyses to examine the nature of trace elements in crude oils. He first used distilled water to extract metals from a California crude. The results for As, Cu, and Zn are summarized in Table 2-3. A considerable portion of arsenic, 37% by weight (this is a direct quote from the paper, the number would be 42 wt% according to Table 2-3), and copper in that crude were extracted to the water phase, while zinc was mostly retained in the crude after the 1:1 distilled water extraction. The results suggest that some oil-soluble arsenic and copper in the crude are hydrolyzable or also water soluble. These hydrolyzable or water soluble arsenic and copper compounds can be extracted to the aqueous phase in the desalting process and be removed from the downstream refining processes.

Table 2-3. Extraction of Trace Elements from a California Crude Oil by Distilled Water (from: Filby, 1975)

Element	Crude Oil (mg/kg)	Extracted Oil (mg/kg)	Aqueous Phase (mg/kg)
As	0.656	0.41	0.276
Cu	0.93	1.03	0.4
Zn	9.32	10.2	1.5

In the same study, Filby (1975) examined the distribution of trace metals including As, Cu, and Zn in a California tertiary oil. The crude was pretreated to remove water and solids from the crude oils by centrifugation and filtration. The crude oil was then separated into asphaltene, resin, and methanol-soluble fractions according to their solubility in methanol and/or pentane. Each fraction was further fractionated based on the molecular weight by gel permeation chromatography. Figure 2-1 shows the preparation steps of Filby's study. The analytical results are briefly summarized as follows.

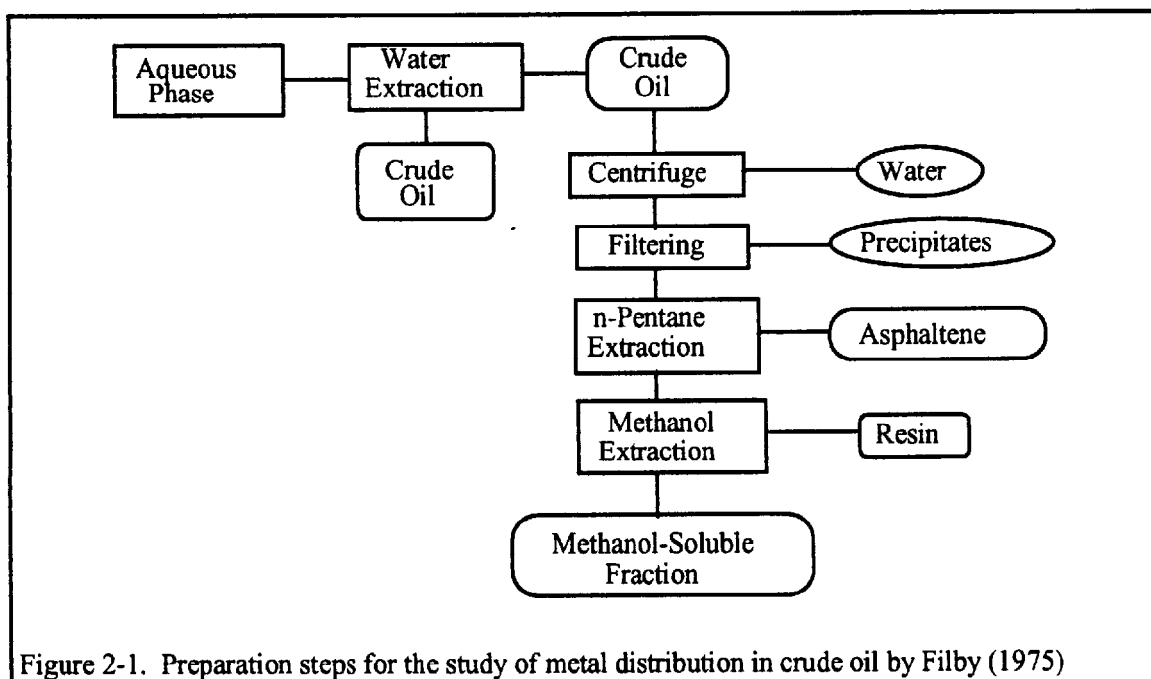


Figure 2-1. Preparation steps for the study of metal distribution in crude oil by Filby (1975)

In the California crude oil sample, an appreciable decrease in the arsenic content was observed when the crude oil went through the centrifugation and filtration steps. It was also shown that residual formation water present in the crude oil could constitute an appreciable source of arsenic, especially for crudes produced from a geological formation with high arsenic in the rocks. The distribution of As, Cu, and Zn in different molecular-weight fractions of the crude oil is tabulated in Table 2-4. The three metals, particularly zinc, tended to concentrate in the heavy fraction, namely the asphaltene. However, asphaltene was only a small portion, 5 wt%, of the crude. The methanol-soluble fraction, on the other hand, accounted for 57.5% mass of the crude. Consequently, about 59 wt%

of arsenic of the crude was in the methanol-soluble fraction. The broad distribution of the metals in all different molecular weight fractions of the crude suggests the presence of a wide variety of organics that may be associated with these trace metals.

Table 2-4. Distribution of As, Cu, and Zn in the components of a California crude oil
(from: Filby, 1975)

Components	Distribution wt% Crude or wt% Components	Arsenic (ppmw)	Copper (ppmw)	Zinc (ppmw)
Methanol-Soluble	57.5	0.546	< 0.5	0.74
M.W. 300-1000	93.8	0.34	---	< 1.0
M.W. > 1000	6.2	5	---	3.5
Resin	37.5	0.29	0.32	8.86
M.W. 300-1000	29.4	0.47	< 0.20	3.31
M.W. 1000-4000	21.2	0.2	< 0.50	11
M.W. 4000-8000	49.4	0.2	1.3	27
M.W. 8000-22000	0	---	---	---
Asphaltene	5	2.25	3.02	109
M.W. 300-1000	11	0.85	0.34	112
M.W. 1000-4000	23.2	0.62	1.5	52
M.W. 4000-8000	50.6	1.9	4	103
M.W. 8000-22000	15.2	6.6	7.2	225

Components	Weight Fraction		
	As	Cu	Zn
Methanol-Soluble	0.59	0.35	0.05
Resin	0.20	0.29	0.36
Asphaltene	0.21	0.36	0.59

2. As, Cu, and Zn in Petroleum Refining Processes

Arsine has been identified to be present in light end hydrocarbon streams ($\leq C_4$), particularly from cracking processes. Poisoning of catalysts has been observed when the light end hydrocarbon streams containing arsenic compounds are used as feedstocks for hydrogenation and reforming processes. Consequently, there have been several studies

conducted to understand the fate of arsenic in the refining processes, which are reviewed below. Presence of copper and zinc in the final gasoline product can also be of concern to the product quality. For instance, trace quantities of copper may promote gum formation through enhancing oxidation or polymerization of some unstable impurities in gasoline. In the refinery, brass (containing copper and zinc) was often used as the material for heat exchanger bundles. Monel (containing copper) was used in some equipment in the alkylation processes. Zinc phosphate or metal zinc were sometimes used as coating primer in some product storage tanks for rust inhibition and cathodic protection. These materials present potential contamination sources of copper and zinc to the refining process streams and final refined products through corrosion or leaching. Consequently, there have been very few studies conducted to track the fate of copper and zinc indigenous to crude oil.

Bergerioux *et. al.* (1979) investigated the distribution of some trace metals, arsenic being one of them, in a Venezuelan crude oil and its subsequent distillation products. The investigation encompassed desalting, primary distillation, and vacuum distillation processes. The products withdrawn from the primary distillation unit in the order of descending volatility were: light naphtha, heavy naphtha, light distillate (kerosene), heavy distillate (light gas oil), atmospheric oil, and residuum. The residuum was further vacuum distilled into light vacuum distillate, heavy vacuum distillate, and pitch fractions. Samples of the crude, the crude after desalting treatment, and the fractionated products from the primary distillation and vacuum distillation units were collected and measured using neutron activation analysis. Table 2-5 summarizes the physical properties (molecular weight and density), flow rate, and arsenic concentration of each sample. About 15 wt% of arsenic in the crude was removed by the desalting treatment. This is consistent with the finding of Filby (1975). Arsenic concentration was below the detection limit (0.7 ppb) for samples of light and heavy naphtha and light distillate. The concentration of arsenic in each fraction increased with increasing molecular weight. The pitch fraction accounted for about 65 wt%, while the heavy vacuum oil contained another 28 wt% of the total arsenic in all the products. A good mass balance of arsenic was achieved, indicating no loss through the distillation process.

In another study, Bergerioux and Sikovsky (1980) examined the fate of some trace metals including arsenic in a feedstock undergoing the catalytic cracking process. The study was carried out in a Montreal refinery. Two identical streams of feedstock, one hot derived

directly from the prior distillation unit and another cold from the storage tank, were cracked in a catalytic cracking reactor. The cracked product was fractionated into 7 fractions. These fractions in the order of descending boiling points were: decantation oil, heavy catalytic oil, light catalytic oil, heavy catalytic gasoline, light catalytic gasoline, C₃-C₄ stream, and gas lighter than C₃-C₄. All samples except the gas and the C₃-C₄ streams were collected and measured for the trace metal contents using neutron activation analysis. The analytical results for arsenic distribution are tabulated in Table 2-6. It should be noted that the arsenic concentration in the feedstock was very low, in the range of 16-18 ppb, to start with. All fractions were shown to contain arsenic. The highest arsenic concentrations were again found in the heavy fractions. Very little arsenic was detected in the catalytic gasoline fractions. The sum of the arsenic in the collected products from light catalytic gasoline to decantation oil accounted for only 5 wt% of the arsenic in the feed. The remaining 95% of the arsenic was either in the C₃-C₄ or the gas streams which were not sampled. It is also possible that some arsenic could have deposited on the catalyst. However, analysis of trace metal contents in the spent catalyst particles was not attempted in the study.

Table 2-5. Distribution of arsenic in the crude oil samples and in the distillation products (from: Bergerioux, *et. al.*, 1979).

Fraction	Density g/cm ³	Average Molecular Weight	Flow Rate metric ton/day	Arsenic Conc. Conc. (ppb)	Net Arsenic Throughput g/day
INPUT					
Raw Crude (CRC)	0.877	----	9480	20.0	189.6
Desalted Crude (CDC)	0.877	----	9480	17.0	161.2
OUTPUT					168.1
Light Naphtha (CLN)	0.709	104	966	< 0.7	----
Heavy Naphtha (CHN)	0.766	124	803	< 0.7	----
Light Distillate (CLD)	0.825	187	1516	< 0.7	----
Heavy Distillate (CHD)	0.865	247	1113	1.3	1.4
Atmospheric Oil (CAO)	0.898	340	485	6.2	3.0
Light Vacuum Oil (CLVO)	0.904	350	616	12	7.4
Heavy Vacuum Oil (CHVO)	0.922	580	1704	28	47.7
Pitch	0.996	> 1000	2261	48	108.5

Table 2-6. Production characteristics, physical properties, and arsenic concentration in the feeds and products of the catalytic cracking unit (from: Bergerioux, *et. al.*, 1980)

Fraction	Density g/cm ³	Average Molecular Weight	Flow Rate metric ton/day	Arsenic Conc. Conc. (ppb)	Net Arsenic Throughput g/day
Hot Feed (HF)	0.887	> 350	2870	18.0	51.66
Cold Feed (CF)	0.887	> 350	715	16.0	11.44
TOTAL INPUT					63.10
Decanation Oil (DO)	1.042	340	126	10.0	1.26
Heavy Catalytic Oil (HCO)	0.973	270	264	1.9	0.50
Light Catalytic Oil (LCO)	0.892	170	831	0.7	0.58
Heavy Catalytic Gasoline (HCG)	0.778	120	735	< 0.7	0.51
Light Catalytic Gasoline (LCG)	0.671	85	618	<0.7	0.43
				SUM	3.29
C3 to C4; Gases, or Catalysts	0.521	NA	NA	NA	(59.81)
TOTAL OUTPUT					63.10

3. As, Cu, and Zn in the Refined Products

Very little information is available in the open literature concerning the trace metal contents of refined petroleum products. Table 2-7 summarizes available data of As, Cu, and Zn in various refined products. Regular and premium gasoline contained almost non-detectable arsenic. One fuel oil was shown to contain 58 ppb of arsenic. Copper concentration was generally higher than arsenic in the refined products.

Table 2-7. Trace metals in refined petroleum products

Petroleum Product	Arsenic (ppm)	Copper (ppm)	Zinc (ppm)	Reference
Regular Gasoline	< 0.04	3.2-6.5	----	Sheilbley (1975)
Premium Gasoline	< 0.01	0.28-3.8	----	Sheilbley (1975)
Diesel	----	1.9	----	Abu-Elgheit <i>et. al.</i> (1981)
Jet Fuel - Type A	----	----	0.56	Sheilbley (1975)
Aviation Gas	----	4.6	----	Sheilbley (1975)
Fuel Oil	0.058	0.3	0.06-0.32	Sheilbley (1975) & Filby and Shah (1975)

Very little information on Zn in the refined products is available, probably due to less concern of zinc on the quality of the products. In fact, some zinc containing compounds are used as anti-oxidant additives in lube oil.

4. Arsenic in Other Fossil Fuels

Arsenic concentrations in other fossil fuels such as coal and oil shale are significantly higher than that in petroleum, due mostly to their biogeochemical origins. The arsenic concentration in crude oils generally varies from less than 10 ppb to a few ppm. In contrast, the concentration of arsenic in 799 coals of varying ranks averaged 15 ppm (US National Committee for Geochemistry, 1980), while Frutcher *et. al.*(1980) reported 44 ppm of arsenic in their oil shale samples. Because arsenic exists in substantially higher concentrations in oil shale and coal than in the petroleum, it has been studied more in the oil shale and coal conversion processes. The information on arsenic gathered from the coal conversion and oil shale retorting processes may provide clues to the fate and possible speciation of arsenic in petroleum refining processes and products. It is therefore reviewed below.

Weiss *et. al.* (1981) studied organometal species in methanol extracts of oil shales using high performance liquid chromatography-graphite furnace atomic absorption spectrometry. Arsenate, a neutral arsenic-containing compound, and phenylarsonic acid were identified.

Shale oil is produced by the retorting process, in which the organic materials in oil shale are subjected to pyrolytic decomposition. Curtin *et al.* (1978) investigated the arsenic distribution in a shale oil after fractionation. They reported that arsenic distributed throughout the boiling range of the shale oil, from less than 204 °C to higher than 482 °C. The highest arsenic concentration, about 52 ppm, was found in the gas oil fraction, especially in the boiling range of 204-260 °C. The distribution of arsenic over the wide range of boiling points suggested the presence of organic arsenic compounds. They also reported that arsenic in the shale oil distillates could be removed by either caustic solution wash or a nickel-molybdenum catalyst guard bed.

Fox (1980) studied the partition of elements in an *in-situ* simulated shale retorting process. Arsenic at ppm level was detected in retort water. The retort water was generated from the condensation of moisture with shale oil. It contained very high levels of organic (e.g., carboxylic acids, organic nitrogen compounds, some phenols) and inorganic compounds. The retort water had a pH in the range of 8-9, and was strongly buffered by ammonium bicarbonate. To better understand the partitioning of some heavy metals including arsenic between the shale oil and retort water, Fox (1980) conducted a leaching study by contacting the raw shale oil with an ammonium bicarbonate solution. The leaching results showed that a higher arsenic concentration was obtained in the ammonium bicarbonate solution than in the retort water. The results suggested that arsenic compounds in the oil phase could also be soluble in alkaline solution and that the solubility of arsenic compounds might be influenced by the presence of other ions.

Shaw et al. (1981) determined the distribution of arsenic in shale oil products by neutron activation analysis. The shale oil was first vacuum-distilled into three fractions: upgraded oil, residuum, and water. The upgraded oil was then subjected to the standard Hempel distillation into naphtha, light distillate, heavy distillate, and residuum. The arsenic concentrations in the shale oil, naphtha, light distillate, heavy distillate, and residuum were 4.6, below detection, 1.4, 4.4, and 12 ppm, respectively. Apparently, arsenic tended to concentrate in the fractions derived from higher distillation temperatures, i.e., the fractions of higher molecular weight.

In their study of the coal conversion process, Fruchter et al. (1980) found that a significant quantity of As and Se were partitioned into the product oil and the process water, possibly due to the anionic nature of their acid forms. Fish et al. (19) found the presence of a neutral arsenic-containing compound, methanearsonic acid, phenylarsonic acid, and arsenate in the process water from a number of coal retorting processes.

5. Summary

The literature shows that arsenic is present widely in petroleum refining process streams and refined products, mostly in very low concentrations. The heavier or higher boiling point fractions tend to contain a higher level of arsenic. Table 2-8 compiles the boiling points of some known arsenic species and light end petroleum products. Even though none of these alkyl arsenic compounds have been positively identified in the refining

process streams or the refined products, the wide range of the boiling points of the organoarsenic compounds suggests that trace arsenic can spread in a wide variety of petroleum products. Arsenic associated with the high molecular weight organometallic compounds is released during the catalytic cracking process, mostly in the form of arsine and other volatile molecules. These volatile arsenic containing compounds are generally retrieved from the fractionation column in the C₂ and C₃-C₄ cuts. The C₃-C₄ stream, if used for the production of alkylate, provides a potential source of arsenic for the gasoline products. Based on the leaching study in shale oil samples, oil-soluble arsenic compounds may also be water soluble, and consequently, partition to tank bottoms upon contact with the aqueous phase (particularly under alkaline conditions).

Copper and zinc appear to concentrate significantly in the heaviest fraction. Since they are not and do not form volatile compounds, they are present at a higher concentration in the pitch fraction. There is very little literature information on the fate of Cu and Zn in the refining processes. Contamination from the process equipment and vessels has been speculated as a major source of Cu and Zn in some refined products.

Table 2-8. Relative boiling points of light end petroleum products and some arsenic compounds

Compounds	Formula	Boiling Point (C)
Ethylene	CH ₂ =CH ₂	-103.9
Ethane	CH ₃ CH ₃	-88.6
Arsine	AsH ₃	-62.0
Propylene	CH ₃ CH=CH ₂	-47.7
Propane	CH ₃ CH ₂ CH ₃	-42.5
Butane	CH ₃ CH ₂ CH ₂ CH ₃	-0.5
Methyl Arsine	CH ₃ AsH ₂	2.0
Dimethyl Arsine	(CH ₃) ₂ AsH	36.0
Trimethyl Arsine	(CH ₃) ₃ As	50.0
Straight Run Gasoline		20-55

B. Analytic Methods

There have been quite a few analytic techniques developed to measure inorganic arsenic, copper, zinc, and selenium in aqueous phase. Details of some of these techniques can be

found in the Standard Methods (Clesceri, *et. al.*, 1989). Many of these techniques use reagents to react with a specific inorganic species of each metal to form colored compounds which are subsequently quantitated by photospectroscopy. For example, inorganic arsenic compounds are first reduced to arsine. Arsine subsequently reacts with diethyldithiocarbamate to form a soluble red complex which is quantified via photometric measurement. To use these techniques to analyze samples containing organometallic compounds, several sample preparation steps such as ashing, digestion, solvent extraction, oxidation, or reduction are taken to convert the organometallic compounds to the desired inorganic species. Inaccurate measurements may occur due to incomplete conversion to the desired inorganic metal species or due to loss of the metals in the process of sample preparation.

The analytical methods developed more recently for metal quantitation use the principles of atomic spectrometry. In contrast to the techniques mentioned in last paragraph, the atomic spectrometric methods are generally applicable to both aqueous and non-aqueous phases. They also offer higher detection sensitivity and less interference. The commonly used techniques include Atomic Absorption Spectrometry (AAS), Graphite Furnace Atomic Absorption Spectrometry (GF-AAS), Atomic Emission Spectroscopy (AES), Atomic Absorption Spectrometry-Hydride Generation (AAS-HG), Inductively Coupled Plasma (ICP) with Atomic Emission Spectroscopy (AES) or Mass Spectrometry (MS). Extraction, digestion and ashing are typical procedures necessary prior to application of AAS type analytic techniques, particularly for low metal concentration conditions. ICP-AES and ICP-MS require less sample preparation and tend to minimize matrix effects and chemical interferences as compared to AAS.

Another technique which has excellent detection sensitivity and requires little sample preparation is neutron activation analysis. Neutron activation analysis applies irradiation onto a sample at a neutron flux of $10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$, and measures the metals by gamma counting based on their isotopes, for example, ^{76}As for arsenic. Neutron activation analysis is primarily employed to measure trace metal contents in hydrocarbon phase.

Successful speciation of the metal containing compounds requires effective separation of the compounds followed by element-specific detection. Liquid chromatography (reversed phase or ion chromatography) and gas chromatography are the most commonly used separation techniques. Both liquid chromatography and gas chromatography coupled

with one of the following detection techniques: AAS, AAS-HG, AES, ICP-AES and ICP-MS, have been successfully applied to the speciation of arsenic and selenium compounds.

Identification of the compounds is generally done by comparing the retention times of the compounds with known standards in a chromatographic column. Arsenic species found in environmental and biological samples include: arsenite (III), arsenate (V), dimethylarsinic acid (DMAA), methylarsonic acid (MMAA), trimethylarsine, trimethylarsine oxide (TMAO), tetramethylarsonium ion, trimethylarsonioacetate (arsenobetaine), 2-trimethylarsonioethanol (arsenocholine), dimethylarsinoylethanol, dimethylarsinoylribosides, and trimethylarsonioribosyl "phospholipid". Some of these arsenic compounds are available commercially, and can be readily used as standards to aid identification. Little literature information exists concerning the speciation of copper and zinc containing compounds.

Other compound specific identification techniques can also be used for speciation. For examples, ^1H NMR and X-ray crystallography techniques have also been used successfully to identify various arsenic compounds such as arsenobetaine, dimethylarsinoylethanol, and trimethylarsine. X-ray diffraction analysis provides high detection sensitivity and complete identification of compounds which possess crystalline structures. Mass spectrometry is capable of providing both qualitative and quantitative information about the atomic and molecular composition of inorganic and organic compounds. Either Field Desorption (FD) or Fast Atom Bombardment (FAB) can be used as the ion source for the mass spectrometer to identify polar compounds containing arsenic element.

Hydride generation technique with appropriate sample preparation has been successfully applied for determination of arsenite, arsenate, monomethyl arsonic acid (MMAA) and dimethylarsinic acid (DMAA) in water, urine, limestone, etc. Hydride generation technique however shows several problems: 1) efficiency of arsine formation is pH dependent and depends on a concentration of NaBH_4 used to generate arsine; 2) molecular rearrangements of arsine take place during the reduction, and 3) heavy metals and nitrate interfere by reducing the sensitivity of detection. With the recent advances in the technologies of chromatography and atomic spectrometry, this technique has not been widely used for arsenic speciation.

Among all the analytic techniques discussed above, inductively coupled plasma-mass spectrometry appears to be the most versatile for the quantitation and speciation of metal compounds. ICP-MS has extremely high sensitivity, minimum matrix effects and chemical interference. It can be used to analyze multiple elements in both the aqueous and hydrocarbon samples with minimum requirement of sample preparation. In addition, speciation studies can be performed using ICP-MS coupled with a LC (Morrin *et. al.*, 1992; Shum *et al.*, 1992) or IC (Karmakar and Tabatabai, 1991; Morita *et. al.*, 1992).

ICP-AES can also be coupled with the liquid separation system (HPLC or IC) for speciation study. The response of the ICP-AES is expected to be a function of the amount of the element injected regardless of the compound composition. In fact, it has been reported that the peak area responses for four arsenic species separated by the ion exchange chromatography were practically the same (Morita *et. al.*, 1979) and were also almost identical with those separated by the ion-pair liquid chromatography (La Freniere *et. al.*, 1987). The detection sensitivity of ICP-AES may depend on the nature of the compounds in cases where a gradient ion-exchange separation is applied, probably due to matrix interference (Spall *et. al.*, 1986). Thus, quantitative analysis with ion-exchange gradient separation will require the use of appropriate standards, and the amount of unknowns can only be estimated. Typical detection limits for these techniques are in 5-100 µg/kg range per individual species with higher sensitivity of detection in ion-exchange separations than in reversed phase ion-pair chromatography.

C. Removal of Arsenic from Hydrocarbons

One way to approach the problem of arsenic, copper, and zinc in the tank bottoms is to execute source control by removing these metals from the hydrocarbons in refining processes. This section provides literature review on the technologies to remove arsenic and copper from the hydrocarbons in the refining processes. No information on zinc removal came out of our literature search.

In general, the processes employed to remove arsenic compounds from gaseous or liquid phase hydrocarbons can be classified into two categories:

- (1) Chemisorption and reaction of arsenic compounds with some specific chemical reagents: These reagents may be used directly or be composited onto solid materials

with high pore volume. In most cases, high temperature and pressure and hydrogen gas were employed to release arsenic from organometallic compounds. The arsenic species were then removed by subsequent chemisorption and reaction. This type of process applies to both liquid and gaseous hydrocarbons.

- (2) Conversion of the arsenic compounds in hydrocarbon phase to oil-insoluble or water-soluble species: These converted arsenic compounds were subsequently removed by a solid-liquid separation process or by aqueous solution extraction. In some cases, specifically prepared solutions were directly applied to the hydrocarbons to extract arsenic compounds without prior treatment.

These processes are briefly described below. Most of these processes are patented. Readers should consult the original patent publication for more detailed information.

Bertolacini *et. al.* (1963) used concentrated sulfuric acid to acidify silica gel particles. The ratio of sulfuric acid to silica gel was 1:1 by weight. The acidified silica gel was then used to treat arsenic-containing hydrocarbon naphtha. This process was not very sensitive to variations in operating temperatures and pressures. The acidified silica gel had a treatment capacity of 50 pounds or more arsenic per ton of silica gel.

Murray and Plagge (1957) showed that arsenic compounds in hydrocarbons could be removed by an alkaline solution of an alkali or alkaline earth metal. For examples, arsenic compounds in naphtha were substantially removed after treating the naphtha with aqueous alkaline solutions including 5% sodium hydroxide, 2 N sodium hydroxide, 1% sodium carbonate, and 20% calcium phosphate solutions.

Appell (1957) composited metal salts with a porous solid support material, and used them to remove arsenic compounds in fractionated petroleum products. The metals could be Cu, Hg, Ag, Pd, Pt, and Au. Salts of strong acid such as sulfates, bromides, chlorides, fluorides, iodides, and nitrates were preferred. Silica gel, alumina, saw dust etc. could be used as the solid support. The process could be applied at ambient temperatures and a wide range of pressures.

Massoth and Young (1974) dispersed a sorbent made of copper or copper oxide on a porous supporting material such as alumina to reduce arsenic in gaseous hydrocarbon.

Temperatures ranging from 80 to 250 °F and pressures ranging from ambient to 350 psig could be employed. It was proposed that arsenic compounds were removed by chemisorption and by formation of copper arsenide. The presence of sulfur compounds in the feedstock interfered with arsenic removal. A very similar process using lead oxide as the sorbent to remove arsenic from gaseous hydrocarbons was described by Carr *et. al.* (1974). The operating conditions were very similar to those described above. The arsenic removal mechanism was hypothesized to be chemisorption and reaction between lead oxide and arsenic with compounds like $Pb_3As_2O_6$ as products. The effectiveness of this sorbent was also impeded by the presence of sulfur compounds.

Wunderlich (1978) used a fixed bed of oxide or sulfide of metals supported on a high pore volume solid matrix to remove arsenic compounds in gaseous or liquid hydrocarbons. The metals could be iron, nickel, and cobalt. Alumina was used as the solid matrix. The process was operated under a reducing environment such as hydrogen gas, at elevated temperatures between 350-850 °F, and under pressures of less than 1000 psig. The feedstock to be treated should not contain higher than 0.1 weight percent water for effective arsenic removal.

Albertson (1984) used elemental sulfur or aqueous sodium hydrogen phosphate or their combination to remove arsenic from arsenic-containing hydrocarbons. The probable mechanism of arsenic removal in this process was the formation of one or more forms of arsenic sulfide precipitates, which was separated from the hydrocarbon being treated. The operating temperature for this application was recommended between 85-120 °C. The arsenic removal for elemental sulfur, aqueous sodium monohydrogen phosphate, and the combination of the two were 55, 30, and 80%, respectively at ambient temperatures. More than 80% arsenic removal was observed when elemental sulfur was applied alone at temperatures above 85 °C.

Arsenic could also be removed by contacting the arsenic-containing hydrocarbon with hydrogen and a contact material such as coke, activated carbon, or clay according to the patent by Schindler and Sze (1984). The contact material provided surface for the arsenic to deposit. The operating conditions of the process were 500 to 850 °F and 350-2000 psig. To dispose of the contact material as non-hazardous waste, iron was added to the arsenic-containing contact material and heated under temperatures above 1200 °F to form

arsenic-iron compound. The arsenic-iron compound was claimed to be stable against further leaching and mobilization into the environment.

Young (1978) blended a hydrocarbon feedstock containing arsenic with oil-soluble nickel, cobalt, or copper-containing additives, and then heated the resulting solution at a temperature above 300 °F. The process converted arsenic to high boiling point oil-insoluble or to water extractable arsenic compounds. The converted arsenic compounds could then be removed by conventional filtration or desalting techniques. The arsenic removal was in the range of 89-96%.

Fenton (1985) proposed to remove arsenic from shale oil using sulfide materials. In this process scheme, shale oil was treated with an aqueous solution of one or more sulfide materials at an elevated temperature, preferably 150-300 °C. The sulfide materials could be hydrogen sulfide, alkali metal and ammonium sulfides (including polysulfides). When hydrogen sulfide was used, arsenic in the hydrocarbon was primarily converted to arsenic sulfide solids, and could be removed by filtration or centrifugation. If alkaline sulfides such as sodium or ammonium sulfide were applied, water soluble thioarsenites and thioarsenates were more likely to form. These water soluble arsenic compounds could be removed from hydrocarbon by extraction with an aqueous phase. The sulfides, however, might cause formation of emulsion in this treatment process, adding undesirable complexity to the operation.

Kitagawa *et. al.* (1984) proposed using metal oxide catalyst to remove arsenic, particularly arsines, in gaseous hydrocarbons such as liquefied petroleum gas (LPG). The metal oxide catalysts could be manganese oxide, copper oxide, or their mixture. By passing the LPG through a packed bed of the metal oxide catalysts under a temperature ranging from ambient to 60 °C and a pressure between 140-280 psig, arsine and methyl arsines could be reacted to manganese arsenide and copper arsenide. These arsenides could be separated from the hydrocarbon phase since they were adsorbed and retained on catalyst surface, or they could be removed by an additional distillation treatment. The removal efficiency was claimed to be greater than 95%.

In the patent of Nowack and Johnson (1986), catalytic sorbents particularly copper chromite was used to remove arsines from gaseous or liquid hydrocarbons, particularly light olefin hydrocarbons. Copper chromite was stabilized by an alkaline earth metal