

Proceedings: Workshop to Identify Promising Technologies for the Treatment of Produced Water Toxicity

HEALTH AND ENVIRONMENTAL SCIENCES

DEPARTMENTAL REPORT NUMBER DR351

JUNE 1996





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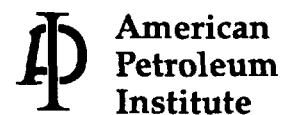
Proceedings: Workshop to Identify Promising Technologies for the Treatment of Produced Water Toxicity

**Health and Environmental Sciences
Departmental Report No. DR351**

PREPARED UNDER CONTRACT BY:

**PARSONS ENGINEERING SCIENCE, INC.
JOHN BOTTS, PROJECT MANAGER
JAMES SALISBURY, ENVIRONMENTAL SCIENTIST
10521 ROSENHAVEN STREET
FAIRFAX, VIRGINIA 22030**

JANUARY 1995



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ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT.

API STAFF CONTACT

Alexis Steen, Health and Environmental Sciences

MEMBERS OF THE API TRE WORK GROUP

Joe Smith (Chairman), Exxon Production Research Company

Kris Bansal, Conoco

Stanley Curtice, Texaco

Philip Dorn, Shell Development Company

Tracy Fowler, Exxon Production Research Company

Jerry Hall, Texaco Research and Design

Sung-I Johnson, Phillips Petroleum Company

Zara Khatib, Shell Development Company

Gary Rausina, Chevron Research and Technology Company

Lawrence Reitsema, Marathon Oil Company

Grateful thanks are also extended to the workshop facilitator, Dr. Eric Snider, P.E. (Clemson University), and to the expert speakers and other workshop attendees without whose participation the workshop would not have been possible.

EXECUTIVE SUMMARY

The American Petroleum Institute (API) sponsored a workshop (October 11-12, 1994) to address produced water toxicity limits and potential treatment methods. Organized by API's Toxicity Reduction Evaluation (TRE) workgroup, the workshop brought together experts in the fields of toxicology and engineering to:

- identify technologies that could potentially be used to reduce the toxicity of produced water (PW) discharges; and
- review and evaluate the technical feasibility and economics of using these treatment technologies on offshore platforms.

The first day of the workshop consisted of presentations on (1) the characteristics and toxicity of produced water, (2) results of tests to identify the causes of PW toxicity using Toxicity Identification Evaluation (TIE) procedures, and (3) engineering constraints impacting offshore produced water treatment. In addition, technical information was presented on five candidate treatment technologies: membrane filtration, carbon adsorption, chemical oxidation, stripping/extraction, and ultraviolet (UV) irradiation.

The Day 1 presentations included the following major points:

- Produced water is variable in composition and flow, but typically has high salinity (9% or greater) and high temperature (up to 140°C) and contains a variety of compounds, including hydrogen sulfide, ammonia, hydrocarbons, carboxylic acids, phenols, heavy metals and radium.
- Phase I TIE procedures have been applied to produced water to characterize the properties of the major fractions contributing to toxicity. This testing indicated that the causes of PW toxicity vary depending on the source. TIE procedures have identified a variety of components contributing to PW toxicity including: particulates, salinity; volatile compounds; extractable organics (acidic, basic, neutral); and compounds affected by pH adjustment. Some individual components were tentatively identified, including ammonia and hydrogen sulfide.
- The integrity of the sample is a concern when testing treatment technologies, because PW characteristics (reduced materials, high pressure, high temperature) may change when exposed to the atmosphere.

- Offshore platforms, as sites for water treatment, have more stringent space, weight, and logistical limitations than onshore treatment facilities.
- Each of the technologies being considered for treatment of produced water toxicity has been successfully applied to onshore treatment of industrial wastes, which are sometimes similar to produced water in composition.

On the second day of the workshop, workgroups evaluated each candidate technology, including a sixth potential technology, biological treatment, identified on Day 1. The workgroup findings and recommendations were summarized in a discussion session at the end of Day 2.

The Day 2 workgroups considered information provided on Day 1 during their evaluations of each technology's applicability for the offshore treatment of produced water. A technology checklist centered attention on the primary areas of interest, including the types of toxicants that might be removed, equipment specifications, operational status and potential for improvement, costs, and recommendations for research.

Strengths of the technologies include their efficiency in removing potential produced water toxicants and, in some cases, the ability to handle variable feed streams. Weaknesses include the generation of waste streams that may require disposal, large size and weight requirements of the technologies, power requirements, and fouling and scaling potential. Treatment costs were compared primarily to the costs of reinjecting the produced water.

Recommendations for additional research were summarized in a final discussion session on the second day of the Workshop. Testing of the effect of emerging treatment technologies on PW toxicity was cited as a primary research need. A closer alignment between TIE procedures and treatability studies of the technologies was recommended. An approach was recommended for testing on several produced waters in the Gulf of Mexico to develop case study information. The suggested approach involved adapting the TIE procedures to more closely approximate the treatment technologies, offshore pilot testing to confirm toxicity reduction, and final testing to develop design and operating criteria.

In summary, the Workshop reviewed technologies potentially capable of treating produced water toxicity in offshore applications. All of the technologies discussed have the potential to be used for produced water toxicity treatment; but, in all cases, further research and bench- and pilot-scale testing is necessary to investigate their effectiveness in this application. To date, none of the technologies have been specifically tested for their ability to reduce toxicity in produced water.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
EXECUTIVE SUMMARY	ES-1
1. INTRODUCTION	1-1
PURPOSE	1-1
ORGANIZATION OF THE PROCEEDINGS	1-2
2. TECHNICAL BACKGROUND	2-1
PRODUCED WATER DISCHARGE	2-1
Toxicity Limits for Produced Water	2-1
Proposed Effluent Toxicity Targets	2-3
Produced Water Toxicants	2-3
Produced Water Composition	2-4
ENGINEERING CONSIDERATIONS FOR OFFSHORE PRODUCED WATER TREATMENT	2-5
3. PROCEEDINGS, DAY 1 - OCTOBER 11, 1994	3-1
OVERVIEW	3-1
DERIVATION, COMPOSITION AND MANAGEMENT OF PRODUCED WATERS	3-2
Source of Produced Water	3-2
Composition of Produced Water	3-2
Properties and Characteristics of Produced Water	3-3
Chemical Additives	3-3
Conclusions	3-4
TOXICOLOGICAL EVALUATION OF PRODUCED WATER/EFFECTS OF ION COMPOSITION ON TOXICITY	3-5
Why Toxicity is Used as a Monitoring Tool	3-5
How Toxicity is Measured	3-5
Toxicity Identification Evaluation	3-6
Ion Composition of Produced Water	3-7



Documents

Document Sharing Hub

TABLE OF CONTENTS (CONTINUED)

<u>Section</u>	<u>Page</u>
PROCEEDINGS, DAY 1 - OCTOBER 11, 1994 (Con't)	
RESULTS OF TOXICITY IDENTIFICATION EVALUATION STUDIES ON PRODUCED WATERS	3-9
Background to the API TIE Study	3-9
Methods	3-9
Results - Produced Water Toxicants	3-10
INTEGRATING TOXICOLOGICAL INFORMATION INTO TREATMENT SELECTION AND DESIGN	3-12
Causes of Toxicity	3-12
Effluent Treatment and Toxicity	3-12
Effluent Characteristics	3-13
On-site Testing	3-13
PRODUCED WATER TREATMENT: ENGINEERING REQUIREMENTS AND CONSTRAINTS	3-14
Background	3-14
Goals of Offshore Production Facilities	3-14
Basic Treatment Requirements	3-15
Cost and space Limitations on Typical Offshore Platforms	3-16
Conclusions	3-17
QUESTION AND ANSWER SESSION	3-18
MEMBRANE FILTRATION	3-20
Background	3-20
Performance of Membranes	3-20
Membranes and Fouling	3-20
Costs of Membrane Treatment	3-20
Experiences with Membranes and Produced Water	3-21
Ideas for the Future	3-21
CARBON ADSORPTION	3-22

TABLE OF CONTENTS (CONTINUED)

<u>Section</u>	<u>Page</u>
PROCEEDINGS, DAY 1 - OCTOBER 11, 1994 (Con't)	
Background	3-22
Pretreatment Requirements	3-22
Typical Specifications and Costs	3-23
CHEMICAL OXIDATION	3-24
Background	3-24
Chemical Reactions	3-24
Experimentation	3-25
Economics of Chemical Oxidation	3-26
STRIPPING/EXTRACTION	3-27
Background	3-27
Removal Efficiency Data	3-27
Problems with Air Stripping of Produced Water	3-28
Design of a Packed Tower	3-28
Costs of Air Stripping	3-29
UV/OXIDATION	3-30
Background	3-30
Experience with UV/Oxidation	3-30
Design of a UV/Oxidation System	3-31
Problems with UV/Oxidation	3-31
Costs of UV/Oxidation	3-31
TECHNOLOGY SELECTION AND COSTS	3-33
Background	3-33
The Produced Water Management Options Model	3-33
Results of the Model	3-34
Miscellaneous Comments	3-34
Conclusions	3-35
ROUNDTABLE DISCUSSION	3-35

TABLE OF CONTENTS (CONTINUED)

<u>Section</u>	<u>Page</u>
4. WORKGROUP SESSIONS, DAY 2 - OCTOBER 12, 1994	4-1
OVERVIEW	4-1
DEFINING THE TREATMENT SCENARIO	4-1
COMPARISON OF THE TOXICITY TREATMENT CAPABILITIES OF THE TECHNOLOGIES	4-3
How well does the technology treat specific chemical groups? ..	4-3
Is additional chemical usage necessary to reduce toxicity?	4-5
COMPARISON OF TECHNOLOGY SPECIFICATIONS	4-6
What are the equipment specifications?	4-6
OPERATIONAL STATUS AND POTENTIAL FOR IMPROVEMENT ...	4-7
What is the technology's current operational state?	4-7
Are there any toxicity reduction performance data?	4-9
What is the potential for technology improvement?	4-11
ADVANTAGES AND DISADVANTAGES OF THE TECHNOLOGIES ..	4-11
What are the advantages and disadvantages of the technologies?	4-13
Describe any side effects from the use of the technology	4-14
Consider the appropriateness, or necessity, of sequential use of treatment technologies	4-14
Cost Evaluation	4-15
5. SUMMARY DISCUSSION AND RECOMMENDATIONS FOR RESEARCH ...	5-1
SUMMARY OF WORKSHOP FINDINGS	5-1
GENERAL RECOMMENDATIONS	5-1
Incorporating Toxicity Reduction Testing in Technology	5-1
Linking TIE Testing to Treatability Studies	5-2
Sampling Procedures	5-3
WORKGROUP RECOMMENDATIONS	5-3

TABLE OF CONTENTS (CONTINUED)

<u>Section</u>	<u>Page</u>
6. REFERENCES	R-1
APPENDIX A	
DETAILED WORKGROUP SESSION DESCRIPTIONS	A-1

LIST OF FIGURES

Figure

3.1 Relative Composition of Produced Water	3-3
3.2 Schematic Diagram of a Fluid Processing System for Offshore Platform ..	3-15
3.3 Oxidation Pathways for Reaction of Hydrogen Peroxide & Organics	3-25
3.4 Schematic of a Packed Tower Air Stripper	3-29

LIST OF TABLES

Table

1.1 API Workshop Agenda	1-3
1.2 List of Participants	1-4
2.1 Critical Dilution Table	2-2
2.2 Critical Dilution Table	2-2
2.3 Effluent Toxicity NOEC Limits and Targets for Toxicity Reduction Study ..	2-3
2.4 Aromatic Compounds in Produced Water	2-6
3.1 Common Test Organisms Used in Toxicity Testing	3-6
3.2 Phase I TIE (EPA Protocol)	3-7
3.3 Manipulations Performed on Produced Water Samples	3-11
3.4 Typical GAC Design Parameters	3-23
3.5 Summary of Roundtable Discussion Comments	3-36
4.1 Toxicity Reduction Checklist used by the Workgroups	4-2
4.2 Summary of Technologies Discussed in Workgroups	4-3
4.3 Comparison of Produced Water Treatment Capabilities	4-4
4.4 Comparison of Technology Specifications	4-8
4.5 Operational Status and Improvement Potential	4-10
4.6 Advantages and Disadvantages of the Technologies	4-12
4.7 Estimated Costs of Technologies	4-17
5.1 Recommendations for Future Research	5-4

Section 1

INTRODUCTION

Produced water is the aqueous phase that comes to the surface along with oil and gas produced from underground formations. At offshore production platforms, produced water is typically treated to remove all but minute amounts of oil and grease and then discharged into the ocean. On December 3, 1993 the U.S. Environmental Protection Agency issued an NPDES General Permit for the western portion of the Outer Continental Shelf of the Gulf of Mexico which included a limit on produced water toxicity. The Permit requires operators to demonstrate that the concentration of discharged produced water at a distance of 100 m from the outfall does not exceed the threshold for chronic toxicity measured in a laboratory test. To assist operators in meeting this limit, the American Petroleum Institute (API) formed a Toxicity Reduction Evaluation (TRE) Workgroup to guide research on produced water treatment for toxicity reduction. As an initial step in their strategy development process, the TRE Workgroup sponsored a workshop to identify promising technologies for the treatment of produced water toxicity.

This Workshop took place on October 11 and 12, 1994 at the South Shore Harbor Conference Center, League City, Texas and brought together a variety of experts in the field of produced water toxicity and its treatment. The Workshop agenda and list of participants are shown in Tables 1-1 and 1-2, respectively.

PURPOSE

The purpose of the workshop was to identify promising technologies that could be utilized on offshore platforms for the treatment of produced water toxicity. To this end, information was presented on produced water toxicity and characteristics, the results of TIEs carried out on produced waters, and the engineering restrictions imposed by offshore platforms. In addition, presentations were given describing five treatment technologies and their applicability to produced water treatment, including cost data. The treatment technologies evaluated were membrane filtration, carbon adsorption, chemical oxidation, stripping/extraction, and UV oxidation. Additional discussion yielded a sixth technology for evaluation, biological treatment.

Having defined the characteristics of produced water, the factors affecting toxicity, and the challenges involved with the offshore treatment of the effluent, six workgroups were assembled to discuss the suitability of the treatment technologies for this application. The aim of these workgroups was to review and evaluate the practicability and the economics of the technologies, and to recommend areas for further research and testing. In addition, the approaches of effluent dilution and reinjection were compared to the treatment options in order to assess the relative applicability of the technologies for achieving compliance with the toxicity limit.

Finally a group discussion was held which summarized the previous discussions and reached conclusions with respect to the offshore treatment of produced water to reduce toxicity.

ORGANIZATION OF THE PROCEEDINGS

These proceedings are organized in a manner similar to the workshop agenda:

Section 2 Provides background material on the subject of produced water and engineering considerations for its treatment;

Section 3 Presents the Day 1 proceedings, including the technical presentations and roundtable discussion;

Section 4 Presents a summary of the Day 2 proceedings, including the workgroup meetings and the final workshop discussion; and

Section 5 Lists the conclusions and recommendations of the workshop.

Appendix A Presents detailed summaries of the workgroup discussions that took place on Day 2 of the workshop.

Table 1-1 API Workshop Agenda

Tuesday, October 11, 1994	
Introductions, Plenary Session and Roundtable Discussion	
8:30am - 9:00am	Registration
9:00am - 9:15am	Introductions and Overview of Workshop Objectives <i>Eric Snider, Facilitator (Clemson University)</i>
9:15am - 9:40am	Derivation, Composition, and Management of Produced Waters <i>Dan Caudle (Consultant)</i>
9:40am - 10:00am	Toxicological Evaluation of Produced Water and Effects of Ion Composition on Toxicity <i>David Mount (National Biological Survey)</i>
10:00am - 10:25am	Results of Toxicity Identification Evaluation Studies on Produced Waters <i>Ted Sauer (Battelle)</i>
10:25am - 10:45am	Integrating Toxicological Information into Treatment Selection and Design <i>Donald Mount (ASCI Corporation)</i>
10:45am - 11:00am	BREAK
11:00am - 11:45am	Produced Water Treatment: Engineering Requirements and Constraints <i>Ken Arnold (Paragon Engineering Services) and Zara Khatib (Shell Development Company)</i>
11:45am - 12:00pm	Question and Answer Session
12:00pm - 1:00pm	LUNCH
1:00pm - 5:00pm	Theory and Practice of Produced Water Treatment Filtration - <i>Brad Culkin (New Logic International)</i> Adsorption - <i>Bill Komegay (Parsons Engineering Science)</i> Chemical Treatment - <i>Alan Bowers (Vanderbilt University)</i> Stripping/Extraction - <i>David Hand (Michigan Technological University)</i> Irradiation - <i>Dan Nolan (Solarchem Environmental Systems)</i> Technology Selection and Costs - <i>Lonny Lawrence (Remediation Technologies)</i>
5:00pm - 5:15pm	BREAK
5:15pm - 6:00pm	Roundtable Discussion on Produced Water Toxicity Treatment Technologies
6:00pm - 6:30pm	Workgroup Assignments and Objectives
Wednesday, October 12, 1994	
Workgroup Sessions and Summary Discussion	
8:30am - 8:45am	Establish Workgroup Objectives <i>Eric Snider, Facilitator (Clemson University)</i>
8:45am - 12:00pm	Workgroup Sessions
12:00pm - 12:10pm	General Meeting <i>Eric Snider, Facilitator (Clemson University)</i>
12:10pm - 1:10pm	LUNCH
1:10pm - 5:00pm	Summary Discussion

Table 1-2 List of Participants

API TRE WORKGROUP MEMBERS	
NAME	AFFILIATION
BANSAL, Kris	Conoco
CURTICE, Stanley	Texaco
DORN, Philip	Shell Development Co.
FOWLER, Tracy	Exxon Production Research Co.
HALL, Jerry	Texaco R&D
JOHNSON, Sung-I	Phillips Petroleum Co.
RAUSINA, Gary	Chevron Research and Technology Co.
REITSEMA, Lawrence	Marathon Oil Co.
SMITH, Joseph	Exxon Production Research Co.
STEEN, Alexis	American Petroleum Institute
WORKSHOP FACILITATORS	
NAME	AFFILIATION
SNIDER, Eric	Clemson University
BOTTS, John	Parsons Engineering Science
EXPERT SPEAKERS	
NAME	AFFILIATION
ARNOLD, Ken	Paragon Engineering
BOWERS, Alan	Vanderbilt University
CAUDLE, Dan	Consultant
CULKIN, Brad	New Logic International
HAND, David	Michigan Technological University
KHATIB, Zara	Shell Development Company
KORNEGAY, Billy	Parsons Engineering Science
LAWRENCE, Lonny	Remediation Technologies (RETEC)
MOUNT, David	National Biological Survey
MOUNT, Donald	ASCI Corporation
NOLAN, Dan	Solarchem Environmental Systems
SAUER, Ted	Battelle Ocean Sciences

Table 1-2 List of Participants (continued)

NAME	OTHER PARTICIPANTS AFFILIATION
BETTLE, Chip	Ecozone
BUZAN, James	Phillips Petroleum Co.
EVANS, Jim	Gas Research Institute
GEORGE-ARES, Anita	Exxon Biomedical Sciences
HAM, Jerry	Department of Energy
HARDY, Greg	Shell Offshore
JOHNSEN, Ståle	Stat Oil
MacNAUGHTON, Michael	Southwest Research Institute
RAY, Jim	Shell
RUBINSTEIN, Ian	Exxon Chemicals Co.
SHANNON, Brian	ARCO Exploration and Production Tech.
SUBCASKY, Wayne	Chevron Petroleum Technology Co.
TAYLOR, Windle	Texas Railroad Commission
TYRIE, Colin	Clean H ₂ O Services
VIDAURRI, Fernando	Phillips Petroleum R&D

Section 2

TECHNICAL BACKGROUND

This section provides background information on the toxicity limitations for produced water, the composition of produced water, engineering considerations for the offshore treatment of produced water, and considerations for treatment of produced water toxicity. This information was provided to the workshop participants to assist in evaluating the toxicity reduction technologies.

PRODUCED WATER DISCHARGE

Toxicity Limits for Produced Water

The NPDES permit governing produced water discharges regards the dilution rate as a function of discharge flow rate, outfall pipe diameter, and the distance (depth difference) between the outfall pipe and the sea bottom (EPA, 1993). The flow rate and pipe diameter are primary factors in determining the physical characteristics of the effluent plume, including the rate of dilution with receiving water. The rate of dilution is greatest if the depth difference between the outfall pipe and sea bottom is large enough so that the effluent plume does not encounter the sea bottom. The Gulf of Mexico NPDES permit considers other factors that influence dilution rates (i.e., effluent salinity and temperature and the current and hydrographic conditions in the receiving water) to be the same for all produced discharges in the Gulf of Mexico.

The Gulf of Mexico NPDES Permit prohibits discharges that result in effluent concentrations at 100 m from the discharge point that are in excess of the NOEC for chronic toxicity to either *Mysidopsis bahia* or *Cyprinodon variegatus* as measured in a 7-day laboratory test. Determination of compliance is a two-step process. Operators first determine the effluent No Observed Effect Concentration (NOEC) using a 7 day chronic toxicity test as specified by EPA (1988). Operators then consult tables in the Permit, shown in Tables 2-1 and 2-2, that give the effluent concentration as a function of flow rate, pipe diameter, and distance between the discharge pipe mouth and the sea floor. The discharge is permitted if the NOEC is greater than the permit table concentration.

Critical Dilution Table 2-1 (Depth Difference 0-4 m)

Critical Dilution Table (December 1993)								
Effluent Concentrations in Percent for Depth Difference 0-4 m								
Discharge Rate (bbl/d)		Pipe Diameter Inches						
Lower Limit	Upper Limit	0-3	3-5	5-7	7-9	9-11	11-16	>16
0	500	0.17	0.17	0.17	0.17	0.17	0.17	0.04
501	1000	0.45	0.40	0.40	0.40	0.40	0.40	0.08
1001	2000	1.39	1.08	1.08	1.08	1.08	1.08	0.16
2001	3000	1.66	1.39	1.32	1.32	1.32	1.32	1.32
3001	4000	1.97	1.60	1.45	1.45	1.45	1.45	1.45
4001	5000	1.94	1.77	1.55	1.55	1.55	1.55	1.55
5001	6000	1.90	1.93	1.66	1.63	1.63	1.63	1.63
6001	7000	1.86	2.07	1.78	1.70	1.70	1.70	1.70
7001	8000	1.81	2.20	1.89	1.76	1.76	1.76	1.76
8001	9000	1.77	2.32	1.99	1.81	1.81	1.81	1.81
9001	10000	1.73	2.43	2.08	1.86	1.86	1.86	1.86
10001	15000	1.56	2.64	2.49	2.16	2.03	2.03	2.03
15001	20000	1.43	2.49	2.85	2.47	2.17	2.17	2.17
20001	25000	1.34	2.39	3.13	2.75	2.42	2.29	2.29

Critical Dilution Table 2-2 (Depth Difference >12 m)

Critical Dilution Table (December 1993)								
Effluent Concentrations in Percent for Depth Difference >12 m								
Discharge Rate (bbl/d)		Pipe Diameter Inches						
Lower Limit	Upper Limit	0-3	3-5	5-7	7-9	9-11	11-16	>16
0	500	0.04	0.04	0.04	0.04	0.04	0.04	0.04
501	1000	0.07	0.07	0.07	0.07	0.07	0.07	0.07
1001	2000	0.11	0.10	0.10	0.10	0.10	0.10	0.10
2001	3000	0.14	0.13	0.13	0.13	0.13	0.13	0.13
3001	4000	0.17	0.16	0.16	0.16	0.16	0.16	0.16
4001	5000	0.21	0.20	0.19	0.19	0.19	0.19	0.19
5001	6000	0.24	0.23	0.22	0.22	0.22	0.22	0.22
6001	7000	0.28	0.26	0.25	0.25	0.25	0.25	0.25
7001	8000	0.32	0.30	0.29	0.28	0.28	0.28	0.28
8001	9000	0.36	0.34	0.32	0.31	0.31	0.31	0.31
9001	10000	0.41	0.38	0.36	0.35	0.35	0.35	0.35
10001	15000	0.28	0.84	0.83	0.81	0.80	0.80	0.80
15001	20000	0.31	1.01	0.99	0.97	0.67	0.67	0.67
20001	25000	1.07	1.15	1.13	1.11	1.09	1.08	1.08

Toxicity to marine organisms from exposure to produced water typically occurs at concentrations above 1% for exposure periods of 24 hours or greater. The 7-day NOEC for PWs from eight Gulf of Mexico platforms ranged from < 0.75 to 7 percent, with an average NOEC of 1.6 percent (Moffett et al 1992). Based on the average NOEC for the Gulf of Mexico produced waters, discharges into shallow water (Table 2-1) will face more difficulty in complying with the NPDES limit (Table 2-2) only the highest flow dischargers or the most toxic effluents will not comply. The great majority of Gulf of Mexico outfalls have depth differences greater than 13 m so that dilution of the plume is not hindered by contact with the sea bottom.

Proposed Effluent Toxicity Targets

The target level for toxicity reduction needs to include a safety factor to ensure that normal variations in effluent toxicity will not result in exceeding the toxicity limit. For discussion purposes a proposed toxicity target can be set at 150% of the appropriate concentration in the permit tables. Table concentrations and target NOECs for three discharge rates are shown in Table 2-3.

Table 2-3. Effluent Toxicity NOEC Limits and Targets for Toxicity Reduction Study

Rate (bbl/day)	Effluent Concentration (%)			
	Table Concentration		Target NOEC	
	Shallow Water	Deep Water	Shallow Water	Deep Water
1,000	0.08	0.07	0.12	0.11
10,000	1.73	0.35	2.60	0.53
25,000	2.30	1.08	3.45	1.62

Produced Water Toxicants

Toxicants in produced water may be present due to either the natural interactions between rock, crude oil, and water in the formation or the chemicals added to produced water during the treatment process. The identification of produced water

toxicants, the chemical targets for toxicity reduction treatment, is the subject of ongoing research. This work has involved the use of TIE procedures, which involve a series of physical or chemical manipulations to isolate or remove certain classes of compounds from produced water. Toxicity tests are then performed on isolated fractions or on manipulated produced water to determine if the manipulations isolated toxicants or reduced the toxicity of the produced water relative to that of the original sample. For example, if bubbling nitrogen through the produced water reduces its toxicity, it can be inferred that there are volatile toxicants in the sample. The results of produced water TIE studies are summarize in Section 3 of these proceedings. The state of understanding of produced water toxicity is not sufficiently well developed to define the targets for toxicity reduction treatment in terms of specific chemical constituents.

Produced Water Composition

The salinity of produced water ranges from essentially fresh to very high (approximately 300,000 ppm TDS). Practical treatment technologies must be able to accommodate a feed stream with an average salinity of 100,000 ppm TDS.

The ionic composition of produced water limits potential treatment technologies to those capable of accommodating a highly saline feed stream with significant hardness. Some of the metallic constituents are of concern as potential toxicants.

The oil and grease content is significant because organic constituents are considered potential toxicants and oil and grease fouls treatment equipment such as membrane filtration units. The oil and grease content of produced water discharges is limited to a monthly average of 29 ppm and a daily maximum of 42 ppm. Excursions in oil and grease levels occur; however, for the purpose of this workshop, potential treatment technologies must be able to accommodate an average oil and grease content of 42 ppm. The susceptibility of treatment equipment to fouling should be considered in evaluating treatment technologies.

Organic constituents of produced water, particularly aromatic compounds, are of concern as potential toxicants (Table 2-4). The ability to remove aromatic hydrocarbons is a factor in evaluating any treatment technology directed at organic constituents.

ENGINEERING CONSIDERATIONS FOR OFFSHORE PRODUCED WATER TREATMENT

Offshore production platforms, as sites for produced water treatment, have space, weight and logistical limitations that are more stringent than those of onshore treatment facilities. These limitations impose additional restrictions on the selection of offshore produced water treatment technologies, beyond those dictated by effluent quality requirements.

Primarily, the design of all produced water treatment facilities must consider the effluent water quality requirements, the expected range of flow rates, the variability of the feed stream composition and cost. However, the offshore environment forces additional factors to be taken into account:

- Deck space and weight capacity are among the key factors that determine the cost of offshore platform construction. Therefore, all process equipment space and weight requirements must be minimized to avoid cost impacts.
- The availability of auxiliary utilities, such as electricity, air and heating media (e.g., steam) are also likely to be limited on existing offshore platforms. If equipment requires these utilities, additional generators, blowers, or heaters may be necessary which will impact costs further. For this reason, it is preferable for treatment technologies to have minimal utility requirements.
- Logistical support requirements are a significant factor in evaluating technology for offshore use. Boat transport provides routine delivery of all consumables (e.g., chemicals, spare parts) and removal of wastes (e.g., filter cartridges). Since the weather may disrupt delivery or pick-up schedules, storage space may have to be provided on the platform for these items.

- Safety considerations may impact the specifications for equipment as, for the offshore environment, equipment must generally meet the electrical requirements for explosion-proof service.
- Finally, many offshore platforms in the Gulf of Mexico are unmanned and, therefore, process equipment may have to function without constant operator control.

In conclusion, the offshore environment poses particular challenges with respect to the engineering and design of treatment equipment. These factors must be considered during the assessment of any treatment technology.

Table 2-4 Aromatic Compounds in Produced Water (source: E&P Forum [1994])

Compound	Gas Platforms	Oil Platforms	Units
Benzene	3-440	4-5	ppm
Toluene	4-145	0.01-2	ppm
Xylenes	8-84	1-7	ppm
Naphthalene	300	66	ppb
Biphenyl	140	4	ppb
Fluorene	7.5	<2	ppb
Phenanthrene	7.25	<2	ppb
Acenaphthene	63.5	<2	ppb
Acenaphthylene	59	<2	ppb
Fluoranthene	4.9	<2	ppb
Anthracene	0.25	<2	ppb
Pyrene	1.05	<2	ppb
Benzo[a]pyrene	<0.1	<2	ppb
Perylene	<1	<.5	ppb
Benz[b]fluoranthene	<1.4	<2	ppb
Benz[k]fluoranthene	<1.1	<2	ppb
Dibenz[a,h]anthracene	<0.1	<2	ppb
Benzo[g,h,i]perylene	<1	<2	ppb
Indeno[1,2,3]pyrene	<.5	<2	ppb
Dibenzothiophene	NA	0.5	ppb

Section 3

PROCEEDINGS

DAY 1 - OCTOBER 11, 1994

OVERVIEW

The following section summarizes the presentations and discussions that took place on Day 1 of the workshop. A range of presentations were given that provided information on produced water toxicity and characteristics, the results of TIEs carried out on produced waters, and the engineering restrictions imposed by offshore platforms. In addition, information was presented describing five treatment technologies and their applicability to produced water treatment, including cost data. A list of the presentations is given below:

- Derivation, Composition and Management of Produced Waters.
- Toxicological Evaluation of Produced Water/Effects of Ion Composition on Toxicity.
- Results of Toxicity Identification Evaluation Studies on Produced Waters.
- Integrating Toxicological Information into Treatment Selection and Design.
- Produced Water Treatment: Engineering Requirements and Constraints.
- Membrane Filtration.
- Carbon Adsorption.
- Chemical Oxidation.
- Stripping/Extraction.
- UV/Oxidation.
- Technology Selection and Costs.

DERIVATION, COMPOSITION AND MANAGEMENT OF PRODUCED WATERS

by Dan Caudle, Ph.D., consultant

Source of Produced Water

Produced water is water that has been in contact with oil or gas underground, and is brought to the surface when the product is extracted. The quantity of produced water varies over the short-term and the long-term. Over the short-term, for various reasons, there can be variations between minus 100% to more than 200% of the nominal flow rate. In the long-term, the produced water flow typically begins at practically nil (<5% of flow) and, over the life of the well, increases until production is 90 to 95% water and very little oil.

Composition of Produced Water

The composition of produced water is also variable from case to case, and over time, although typically it is mostly water containing salts and some organics (see Figure 3-1).

Common compounds found in produced water include:

- Salts (mainly sodium chloride, but other common cations and anions are present also).
- Inorganics (e.g. hydrogen sulfide, ammonia).
- Dissolved organics (e.g. benzene, toluene, xylene).
- Non-hydrocarbon organics (e.g. carboxylates, phenolates, nitrogen-containing compounds).
- Heavy metals.
- Radium.

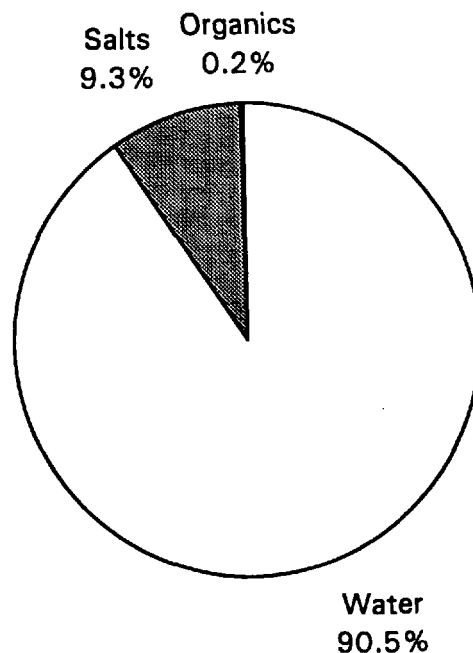


Figure 3-1 Relative Composition of Produced Water

Properties and Characteristics of Produced Water

A number of produced water components react with air and so consequently, when the water is brought to the surface, chemical changes may occur if it is exposed to the atmosphere. This is an important property to take into account during sampling or storage. Additionally, most of the organic constituents of produced water are very similar in character which makes treatment of specific organic contaminants difficult. Produced water may also contain traces of radium, although this does not pose any significant risk to health.

Chemical Additives

A variety of treating chemicals may be used in production systems in order to achieve the quality goals for the oil and/or gas being sold, or to protect equipment from failure. Commonly, these chemicals are:

- Corrosion inhibitors (typically amines, amides) or oxygen scavengers.
- Hydrate inhibitors (methanol and/or glycols).
- Scale inhibitors.
- Biocides.
- Emulsion breakers.
- Coagulants and/or flocculants.
- Antifoams (usually silicon compounds).

Conclusions

Produced water is variable in terms of quantity produced and in composition, over both the short- and the long-terms.

The general composition of produced water is mainly water containing salts and small quantities of various organic compounds. A variety of treatment chemicals may also be found in produced water.

TOXICOLOGICAL EVALUATION OF PRODUCED WATER/EFFECTS OF ION COMPOSITION ON TOXICITY

by David Mount, Ph.D., National Biological Survey

Why Toxicity is Used as a Monitoring Tool

There are "too many chemicals" to perform sufficient background testing to establish environmental limits for everything. In addition, even though these limits could be established, interactions among chemicals potentially alter their effects and the limits might become irrelevant. Also the bioavailability of chemicals varies in the environment which has an effect on their toxicity. Therefore, measurement of the whole toxicity of an effluent is a good method by which to take account of all of the above factors.

How Toxicity is Measured

Acute (short-term) and chronic (long-term) toxicity are both measured by evaluating the response of a test organism that is exposed to the potentially toxic effluent. Toxicity tests on various organisms are used to establish the toxicity of the effluent which is described using values such as the "median lethal concentration" (LC_{50}). The LC_{50} describes the concentration at which 50% of the test organisms would be killed in a specified time period.

In the case of chronic tests, the most common terms that are used to describe toxicity are the "No Observed Effect Concentration" (or NOEC) and the "Lowest Observed Effect Concentration" (LOEC). These concentrations are determined by the concentration of effluent at which no toxic effects are observed (for NOEC) or, the lowest concentration at which a toxic effect is observed (for LOEC). In either case this effect could be something such as inhibited growth or inhibited reproduction; not just a lethal effect.

Another term used in toxicity studies is the “toxic unit”. All of the aforementioned terms refer to concentrations of the tested substance and, therefore, are counterintuitive (i.e. as toxicity increases, the LC_{50} , NOEC or LOEC decrease). Toxic units are calculated by taking the inverse of the LC_{50} so, for example, an LC_{50} of 50% converts to 2 toxic units and an LC_{50} of 25% converts to 4 toxic units. This better reflects that a solution with an LC_{50} of 25% is theoretically twice as toxic as one with an LC_{50} of 50%.

Typical marine test organisms are the mysid shrimp (*Mysidopsis bahia*) and the sheepshead minnow (*Cyprinodon variegatus*). Table 3-1 lists additional common test organisms.

Table 3-1 Common Test Organisms used in Toxicity Testing

Marine	mysid shrimp (<i>Mysidopsis bahia</i>) silverside (<i>Menidia sp.</i>) sheepshead minnow (<i>Cyprinodon variegatus</i>)
Freshwater	water flea (<i>Ceriodaphnia dubia</i>) fathead minnow (<i>Pimephales promelas</i>) water flea (<i>Daphnia magna</i>)

Toxicity Identification Evaluation

Despite being a useful tool for the measurement of complex effluents, toxicity measurement has a drawback which is that it is generic (i.e. it gives no indication of the cause of the toxicity). Methods, collectively called Toxicity Identification Evaluation, have been developed to allow the classification of the toxicants within a sample.

The TIE is split into three phases (Phase I - characterization, Phase II - identification, and Phase III - confirmation) and involves a series of physical and/or chemical

manipulations of the test sample, followed by toxicity tests. The toxicity of the manipulated samples can then be compared to the toxicity of the original sample to infer information concerning the physical and/or chemical properties of the toxicant(s). The Phase I TIE tests (EPA Protocol) and the toxicant groups they address are shown in Table 3-2.

Table 3-2 Phase I TIE Tests (EPA Protocol)

Manipulation	Toxicants Addressed
Aeration	Volatile compounds
Filtration	Solids, emulsions, surfactants
Solid-phase Extraction (SPE)	Non-polar Organics
Extreme pH Adjustment (acidic and basic)	Irreversibly degradable compounds
EDTA Addition	Metals
Thiosulfate Addition	Oxidants, metals
Graduated pH Adjustment (acidic and basic)	Ammonia, metals, sulfides

Ion Composition of Produced Water

For marine organisms, toxicity can be caused not only by excessive concentrations of certain ions, but also a deficiency of some ions. With respect to ion deficiency, marine organisms are most sensitive to deficiencies of calcium and potassium; toxicity can occur when concentrations of these ions fall below 50% of their normal concentrations in seawater. However, because compliance with NPDES permit limits

is based on critical concentrations below 5%, ion deficiency should not generally be a compliance issue. Problems with toxicity compliance because of ion excesses are theoretically possible, but would only be likely in produced water containing extremely high concentrations of certain ions, particularly calcium and potassium.

Although ion imbalances are not likely to be compliance issues themselves, understanding of ion toxicity may be very important to interpretation of TIE test results where changes in relative toxicity are being assessed. GRI research on ionic toxicity to marine organisms is ongoing and should be available to complement evaluations of produced water toxicity that may be pursued as a result of this workshop.

RESULTS OF TOXICITY IDENTIFICATION EVALUATION STUDIES ON PRODUCED WATERS

by Theodor Sauer, Ph.D., Battelle

Background to the API TIE Study

An API study, started in 1990, has performed TIEs on low and high-salinity produced waters from production facilities in the United States. The objectives of this study were to investigate different methods of isolating toxicants from produced waters, to evaluate toxicity test organisms suitable for testing low and high salinity effluents, and to identify major components of fractions contributing to produced water toxicity.

Methods

Two types of TIE manipulation were performed on the effluent samples: (1) toxicity reduction manipulations; and (2) toxicity isolation manipulations. The test procedures are summarized in Table 3-3. The toxicity reduction manipulations involve standard TIE fractionation procedures as described in the previous section. The reduction manipulations (e.g. filtration, aeration) are performed on the sample after pH adjustment. The produced water treated by these manipulations is submitted for toxicity testing to determine how the its toxicity compares with that of the original sample. A observed reduction in toxicity following manipulation indicates that a toxicant has been removed by the manipulation. For example, if filtration at basic pH reduces toxicity, it can be inferred that a toxicant in the sample has the characteristic that it can be removed by filtration under basic pH conditions.

In toxicity isolation manipulations, a fraction of the produced water is isolated by solvent extraction and tested for toxicity. The detection of toxicity in the isolated fraction indicates that a produced water toxicant, such as an organic compound, is present that can be removed by solvent extraction.

Both 24-hour and 48-hour acute toxicity tests were performed on whole and fractionated produced water samples. The organisms used for testing low salinity produced waters were *Ceriodaphnia dubia* (Daphnid) and *Pimephales promelas* (Fathead Minnow). The organisms used for testing high salinity produced waters were *Mysidopsis bahia* (Mysid shrimp), *Cyprinodon variegatus* (Sheepshead minnow) and *Arbacia punctulata* (sea urchin).

A series of water quality analyses (e.g. salinity, pH, dissolved oxygen, ammonia, anion and cation composition, oil and grease) were performed on the effluent samples to aid in interpretation of the TIE results.

Results - Produced Water Toxicants

The produced water TIEs showed that the compounds contributing to the effluent toxicity are diverse. No more than two types of compound were identified as potential toxicants for any individual produced waters tested. The following compounds were identified as potential toxicants in the effluent samples:

- Salinity.
- Materials removed by pH adjustment.
- Organics: acidic, neutral or basic compound extraction (ACE, NCE, or BCE) fractions.
- Volatile compounds, including H₂S.
- Particulates removed by filtration at initial pH or pH 11.
- Ammonia.

Table 3-3 Manipulations Performed on Produced Water Samples

Toxicity Reduction Manipulations	
Fractionation Type	Objectives
pH adjustment at pH 3 and 11	Determination of the effect of pH adjustment in fractionations; provides a baseline for pH adjusted fractionations; and addresses issue of increased ionic strength and chemical reversibility.
Aeration with N ₂ at initial pH (pH i), and pH 3 and 11	Removal of volatile compounds under initial, acidic, and basic pH conditions without the presence of oxygen.
Aeration with air at pH i, 3 and 11	Removal of volatile and oxidizable compounds under initial, acidic, and basic pH conditions.
Filtration at pHs i, 3 and 11	Removal of particulates (with a filter) under initial, acidic, and basic pH conditions.
Graduated pH test at pH 6, 7 and 8	Determination of the possible presence of ammonia.
Toxicity Isolation Manipulations	
Fractionation Type	Objectives
Acidic organic compound extraction (ACE) at pH < 2.	Isolation of acidic organic compounds.
Basic organic compound extraction (BCE) at pH > 12	Isolation of basic organic compounds.
Neutral organic compound extraction (NCE)	Isolation of neutral organic compounds.

INTEGRATING TOXICOLOGICAL INFORMATION INTO TREATMENT SELECTION AND DESIGN

by Donald Mount, Ph.D., AScl

Causes of Toxicity

The causes of toxicity may be non-specific (not necessarily related to a single, specific cause). This can lead to challenges in terms of treatment for a number of reasons. An important point to note is that just because something is present in toxic concentrations does not necessarily mean that it is the source of the toxicity. For example, heavy metals may be present in high concentrations but they may be chelated by organic compounds so that they would be unavailable. Therefore they would appear to be non-toxic under these conditions. Additionally, compounds may have a toxic and a non-toxic form (e.g. ammonia and the ammonium ion) which will change under different environmental conditions.

Effluent Treatment and Toxicity

Treatment may remove the major cause of toxicity but then alter the characteristics of the effluent so that another component becomes toxic. For example, organic carbon is a good chelating agent and will complex with metals to make them unavailable (and non-toxic) while it is present. A treatment process designed to remove ammonia may end up removing organic carbon as well, which consequently results in the metals being made available and, therefore, becoming toxic.

It is important to note, therefore, that when an effluent is treated its characteristics will change and these changes may have an effect on the ultimate goal of the treatment, which is to remove toxicity. The treatment chemicals may also have a detrimental effect on the toxicity of the effluent. This is one of the reasons why bench-scale testing is extremely important. Often it is considered that the TIE process is only carried out initially and the TRE is performed only as remedial action and,