

**STUDY TITLE:** Deepwater Program: Literature Review, Environmental Risks of Chemical Products Used in Gulf of Mexico Deepwater Oil & Gas Operations

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CONTRACT NUMBER: 01-98-CT-30900

SPONSORING OCS REGION: Gulf of Mexico

APPLICABLE PLANNING AREA: Gulf of Mexico

FISCAL YEARS OF PROJECT FUNDING: 1998; 1999; 2000; 2001

COMPLETION DATE OF REPORT: January 2001

COSTS: FY 1998: \$25,553; FY 1999: \$93,398; FY 2000: \$228,421; FY 2001: \$19,935

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KEY WORDS: Gulf of Mexico; deepwater; chemical inventory; chemical storage; ecological risk; spill modeling; deepwater biology

**BACKGROUND:** Chemicals have been used in offshore Gulf of Mexico (GOM) oil and natural gas exploration and production (E&P) since development of the offshore resources over a half a century ago. From 1947 to 1985, E&P activities focused on the shallow waters of the continental shelf. Since the mid-1980s, however, the pace of exploration and development in the deep waters of the GOM has accelerated rapidly. By the end of 1999, approximately 1,200 wells had been drilled in water depths exceeding 1,000 ft (305 m) (Minerals Management Service, May 2000). Moreover, production from these deepwater wells has now surpassed production in shallow water, despite the fact that only 4% of all producing fields in the GOM are in deepwater.

**OBJECTIVES:** (1) Establish a baseline inventory of the chemical products, compounds, and mixtures in current use by operators in the GOM, with emphasis on deep waters (over 1,000 ft. or 305 m); (2) estimate the amount of such chemicals expected to be used as exploration in the GOM increases, with emphasis on deep waters; (3) locate and collect technical information on chemical volumes in typical GOM operations; (4) develop conceptual models using a range of chemical spill scenarios

and predicted impacts as a result of these spills; (5) develop an inventory of types and amounts of hazardous substances stored, handled, transferred to, and used on offshore oil and gas facilities in all water depths.

**DESCRIPTION:** An inventory of chemicals used in the Gulf of Mexico was compiled based on data received from three major energy companies operating in both the shallow and deep waters of the Gulf of Mexico, annual reports provided in World Oil magazine, MSDS sheets, and a review of Hudgins' 1991 report on chemical usage in the North Sea. For each of four chemical classes two tables were developed. The first table describes the functional categories within the class and the second lists the products within each chemical class. This data set establishes a searchable chemical inventory database that includes information on chemical products; chemical handling, physical and chemical properties and toxicological data for selected chemicals and/or products.

Models were developed for offshore E&P operations to estimate the volume of chemical transported, stored, and expected to be used at any one time in the Gulf of Mexico (GOM) as follows: (1) data was provided by three major operators in the GOM and their chemical suppliers (total of eight), (2) the data was unitized to yield average volumes or concentrations for each operational unit (well or production amount), (3) the unitized data were multiplied by the corresponding number of wells or fluid production data to extrapolate total volume estimates for the entire GOM.

A subset of representative chemicals used in the deepwater and shallow water was selected for detailed study based on the following criteria: chemicals used offshore in high volumes; potential impact on the environment and factors affecting fate and transport. A total of 17 spill scenarios was developed and modeled using Applied Science Associates' (ASA) chemical spill model CHEMMAP. Sixteen spill scenarios were modeled using shallow water data and one spill scenario was modeled in deepwater. The shallow water current data were obtained from measurements made by Texas A&M University as part of the LATEX program. For each of the chemicals modeled, habitat areas exposed to peak concentrations or mass loadings within range intervals were tabulated. These peak exposure concentrations were compared against acute toxicity data to estimate the potential impact to the environment.

**SIGNIFICANT CONCLUSIONS:** The results of this analysis indicate a potential for impact from a release of either zinc bromide or ammonium chloride. The modeled impacts for zinc bromide were predicted based on a 45,000 gallon release to the environment, a predicted maximum exposure concentration of greater than 1ppm for at least one hour in an area of 11 million m<sup>2</sup> (11 km<sup>2</sup>, volume of 11 million m<sup>2</sup> x 114 m deep = 1,254 million m<sup>3</sup>) around the spill site and an acute 48-hr LC50 toxicity threshold for *Ceriodaphnia dubia* (freshwater crustacean) of 0.5 mg/L. While a spill of ammonium chloride was not modeled, a review of the chemical's structure and properties indicate that it would behave similarly to potassium chloride. Utilizing the modeled maximum predicted exposure concentrations of potassium chloride as a surrogate for ammonium chloride resulting from a potential release of 4,700 kg, a comparison with the LC-50

marine toxicity threshold of 250 mg/L for *Salmo salar* (Atlantic salmon) was conducted that indicates a positive potential for environmental impact. Since the analysis was conducted by proxy, this predication must be qualified as only an indicator of potential risk and the need for a more focussed study on the effects of ammonium chloride on the marine environment.

**STUDY RESULTS:** Chemicals perform critical functions during drilling; cementing; well completion, stimulation, and workover processes; and producing processes. In offshore operations, chemicals fall naturally into four major classes: (1) drilling fluid chemicals, (2) cementing chemicals, (3) completion, stimulation, and workover chemicals and (4) Production-treating chemicals. The liquid and solid drilling fluid chemicals used in the highest quantity in the GOM are: *Shale Control Inhibitors* (liquid)– 1,210,000 gal. (shallow water); 763,000 gal. (deepwater); *Weighting Materials* – 326,000,000 lbs. (shallow water); 372,000,000 lbs. (deepwater); and *Shale Control Inhibitors* (solid) – 6,660,000 lbs. (shallow water); 14,000,000 lbs. (deepwater). The cementing chemicals used in the highest quantity in the GOM are: *Basic Cements* – 203,000,000 lbs. (shallow water); 18,500,000 lbs. (deepwater) *Silica* – 14,100,000 lbs. (shallow water); 1,780,000 lbs. (deepwater) *Extenders/density-reducers* – 3,890,000 lbs. (shallow water); 365,000 lbs. (deepwater). Except for the chemically inert substances such as sand and ceramic proppants the completion, stimulation and workover chemicals used in the highest quantity in the GOM are acids and brine solutions: *Water-based Completion Fluids* – 16,300,000 gal. (shallow water); 760,000 gal. (deepwater), specific chemical amounts were: 9,110,000 gal. of calcium chloride (shallow water); 426,000 gal. (deepwater) and 4,660,000 gal. sodium chloride (shallow water); 218,000 gal. (deepwater); *Hydrochloric Acid* – 2,520,000 gal. solution containing 2,760,000 lbs. HCl (shallow water); 94,100 gal. solution containing 103,000 lbs. HCl (deepwater); *Ammonium Chloride Overflush* – 2,340,000 gal. of 5% solution containing 989,000 lbs. of ammonium chloride (shallow water); 87,400 gal. of solution containing 37,000 lbs. of ammonium chloride (deepwater). The production-treating chemicals used in the highest quantity in the GOM are: *Hydration Inhibition Chemicals (Methanol)* – 5,420,000 gal. (total); *Corrosion Inhibitor* – 2,500,000 gal. (total) and *Hydration Inhibition Chemicals (Glycols)* – 1,460,000 gal. (total). As part of this study, the types and volumes of hazardous substances used, handled, and stored in offshore E&P operations were identified. Hazardous chemicals were defined as those substances listed in the U.S. Code of Federal Regulations (CFR) – Chapter 40, Protection of the Environment, Part 116, that designates hazardous substances per the Clean Water Act. Only seven hazardous substances were found to be stored in amounts exceeding reportable quantities; sodium hydroxide, potassium hydroxide, zinc bromide, diethylamine, toluene, xylene, and naphthalene. Twenty-one chemicals were selected for detailed study based on volume estimates, screening-level toxicity data and professional judgement. For each of the selected chemicals a detailed chemical profile was developed to obtain a more definitive characterization of their use, storage, and potential for environmental impact. In addition, spill scenarios were developed and modeled for seventeen of the twenty-one profiled chemicals using Applied Science Associates' (ASA) chemical spill model CHEMMAP. As part of the risk characterization, the results of the modeling effort were integrated with the toxicity data collected for the chemical profiles. The results of

this analysis indicate that a potential for impact exists for both zinc bromide and ammonium chloride.

**STUDY PRODUCTS:** Arthur D. Little, Inc. 2001. Deepwater Program: Literature Review, Environmental Risks of Chemical Products Used in Gulf of Mexico Deepwater Oil & Gas Operations, Volume I: Technical Report and Volume II: Appendices. OCS Study MMS 2001-011 and MMS 2001-012. A final report to U.S. Department of the Interior, Mineral Management Service, Gulf of Mexico OCS Region, Metairie, LA Contract No. 01-98-CT-30900. Volume I: Technical Report 343 pp; Volume II: Appendices 382 pp.

Arthur D. Little, Inc. 2001. Deepwater Program: Literature Review, Database of Chemical Products Used in Gulf of Mexico Deepwater Oil & Gas Operations. A Microsoft Access database submitted to U.S. Department of the Interior, Mineral Management Service, Gulf of Mexico OCS Region, Metairie, LA Contract No. 01-98-CT-30900.

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