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Mixing and Separation Device for Continuous Flow Bioassays with Coal Liquids

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Efforts to increase United States' use of synthetic fuels, such as those derived from coal liquefaction, require examining potential toxicity of coal liquids that may eventually be released to the aquatic environment. Evaluation of potential long-term ecological effects must consider organism response to chronic exposure regimes. Since maintaining constant levels of the water soluble fraction (WSF) of coal liquids is complicated by presence of easily biodegradable phenolic compounds (DEGRAEVE et al. 1980), and since problems with low oxygen levels may occur with static tests, flow-through test systems must be employed. A serious problem with continuous flow studies of crude petroleum oils has been obtaining a consistent WSF. The test solution may contain dispersed oil and the character of the WSF may change during the testing period (CRADDOCK 1977).

Although, batch-prepared WSFs of solvent refined coal (SRC) II materials were adequate for short-term continuous flow or static tests, a system was needed that would generate a stable WSF for long-term continuous flow bioassays. We developed a method to generate a reproducible stock solution for exposing aquatic organisms to sublethal concentrations of coal liquid WSFs under flow-through conductions. Our apparatus extracts a primary WSF from a 2.9:1 blend of middle to heavy SRC II distillate, while separating and removing dispersed and floating insoluble materials. The WSF is efficiently extracted, thus reducing costs associated with waste treatment of the potentially hazardous materials.

METHODS

System Design and Rationale

Although it is our intention to apply this same mixing principle to other complex organic materials, the present paper illustrates methodology developed with a SRC II liquid[1]. Primary extraction of soluble SRC II liquid by water is accomplished by

[1]The SRC II liquid was obtained from a pilot plant and may not represent demonstration facility operations.

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simultaneously introducing deionized or filtered river water and SRC II to a baffle-filled glass tube (Fig. 1). Primary dilution water is introduced to the mixing column via a stainless steel line (6mm diameter), needle valve and solenoid valve with line pressure at about 4-5 psi. SRC II material is metered into the column through a 1 mm ID teflon line by an Eldex series A high pressure precision pump (Model #A-30-S). The raw toxicant line is inserted directly inside the water line so that the SRC II liquid contacts the primary dilution water before further mixing in the baffle tube.

The resultant water/oil emulsion flows directly from the bottom of the baffle tube to the initial compartment of the secondary mixing chamber. The solution then passes over a baffle into a second compartment. Solution level in the secondary mixing chambers is maintained below the center baffle so that overflow facilitates further mixing of oil and water. The oil/water mix then flows to the primary settling and separation partition through a hole in the tertiary mixing chamber wall. Solution level in the primary partition is maintained about 25 mm below this outlet to allow for secondary overflow mixing.

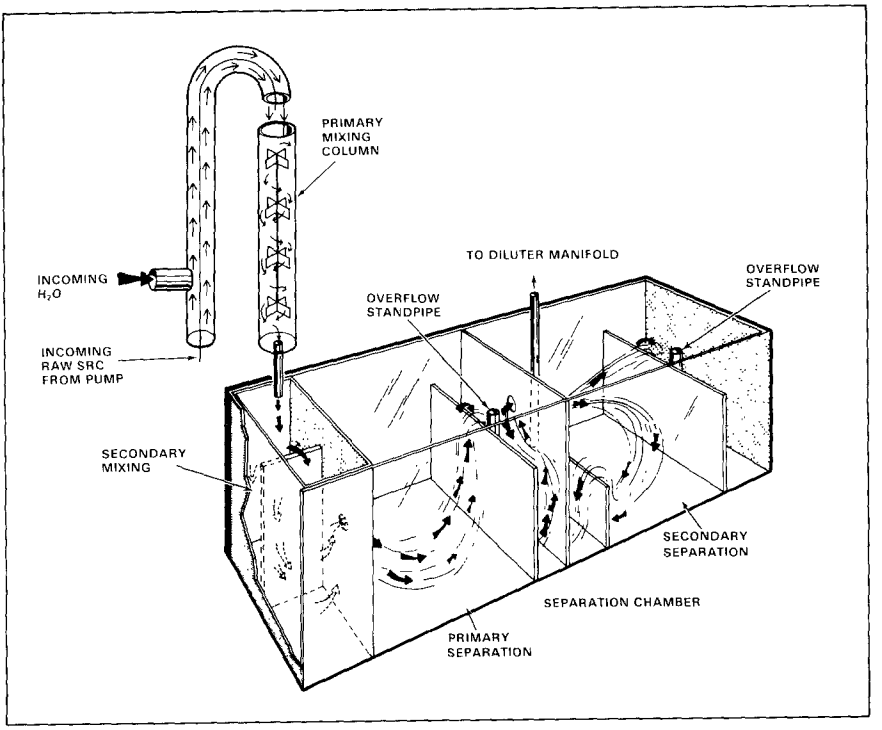

Fig. 1. Mixing and separation ppparatus including inflow and outflow lines and pattern of flow within the system

Oil/water from the primary separation partition enters near the surface of the secondary partition. Inflow current tends to cross the surface of the secondary partition to the overflow where more oil droplets are removed from the system. Settleable droplets are forced toward the surface by a low baffle at the upstream end of the separation chamber. The low baffle also prevents most oil droplets from entering the delivery tube. Secondary separation occurs because two baffles are arranged to provide laminar surface flows with subsurface currents. The baffles retain the oil/water dispersion long enough to allow insoluble oil droplets to rise to the surface and be removed through overflow stand pipes.

Final test solution is delivered from the upstream end of the secondary separation chamber to a dilution chamber or directly to the diluter manifold with an FMI lab pump. The WSF is then diluted to appropriate test concentrations as required to establish the range of toxic response.

Operation

Initial flow rates were based on estimated toxicant concentrations needed to produce sublethal effects and by system capacity. Incoming dilution water was maintained at 60 ml/min with SRC II liquid flows set at 0.4 ml/min. Flows of WSF to the dilutor were adjusted to 44 ml/min, resulting in 16 ml/min waste.

At the highest concentrations tested, the WSF was pumped directly to a toxicant manifold with outlets for excess floating oil discharge and dripper arms for toxicant flow adjustment. Dilution water flows were near 1000 ml/min. Because a highly concentrated stock solution is generated, maintenance of low toxicant flows for chronic effects tests was difficult. Addition of a primary dilution chamber prior to the toxicant manifold may be required to control flows at low test concentrations. A schematic of the entire system is shown in Fig. 2.

System Monitoring

The reproducability of the system was evaluated by frequent monitoring of total organic carbon (TOC) and phenols in the WSF prior to dilution. In addition a more detailed characterization of the WSF was done to quantitate specific phenols and aromatic hydrocarbons.

Concentrations of total phenols in the WSF were estimated by a rapid dye photometric assay. (APHA 1975). Concentrations of SRC II material in the WSF were measured as total organic carbon by direct aqueous injection in a Beckman 915 B carbon analyzer.

RESULTS AND DISCUSSION

SRC II concentrations in the WSF remained at constant levels over the duration of a 21-day test. Mean TOC concentrations of

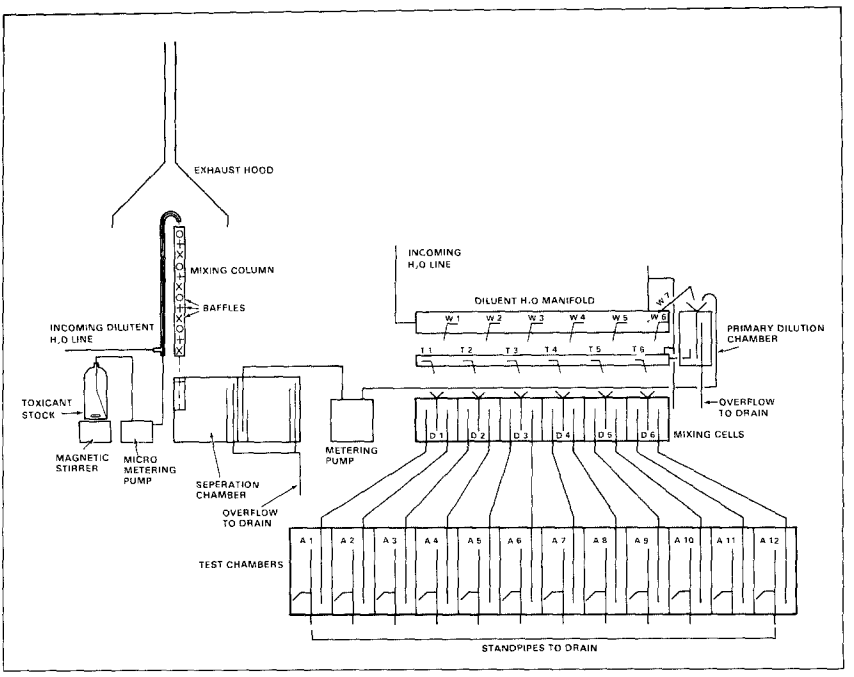

Fig. 2. Schematic of the entire system including mixing and separation system, dilutor system, and test aquaria.

660 ppm were obtained, of which 415 ppm were accountable as dye complexible phenols. Similar results were obtained from a preliminary test series in which SRC II liquid and primary dilution water flows were each increased nearly 3X those reported here. At lower contact flows (dilution flow about 10% less) total carbon values ranged to 890 ppm with dye complexible phenols averaging 459 ppm.

A comparison of phenol distribution obtained with the WSF obtained from our mixing and separation system and with the WSF from a batch mix (STATES et al. 1980) is shown in Table 1. Relative composition is similar in both mixtures. Phenol, C_2 phenols, and cresols contribute >78% of the organic carbon in each mix.

Chemical monitoring showed daily variation in stock solution was minimal. Therefore, we only assayed primary toxicant concentrations daily (5x/wk) during the 3 wk test period. Coefficient of variation (CV) was lowest in the primary stock or WSF (3.8%), but CV increased at each point a river water dilution was made (Table 2). Toxicant levels (as indicated by dye complexible phenol concentrations) decreased from the final mixing cells to the aquaria. Actual organism exposure levels were about 15% less in

TABLE 1

Comparison of phenol distribution between the mix-and-separation apparatus WSF and a batch-prepared WSF.

Phenol class	Flow-through mg/ℓ	Flow-through % total	Batch mg/ℓ	Batch % total
Phenol	140.3	15.3	162.1	16.4
Cresols	320.5	35.0	367.0	37.1
C_2 Phenols	255.0	27.8	273.8	27.7
C_3 Phenols	84.8	9.3	85.9	8.7
C_4 Phenols	31.1	3.4	14.9	1.5
Indanols	47.3	5.2	50.7	5.1
C_5 Phenols	1.2	0.1	1.3	0.1
C_1 Indanols	26.1	2.9	24.4	2.5
C_2 Indanols	9.6	1.0	7.9	0.8
Totals	915.9	100.0	988.0	99.9

TABLE 2

Assayed and calculated phenol concentrations in primary stock, mixing cells, and test aquaria. Values given are means ± S.D. (n=15).

	Total phenols by photometry (mg/ℓ)	Calculated phenols[1] (mg/ℓ)
Primary stock	414.5 ± 15.8	
Mixing cells		
high x_1	1.08 ± 0.19	1.19
x_2	1.14 ± 0.18	1.19
low y_1	0.39 ± 0.09	0.40
y_2	0.38 ± 0.07	0.40
Aquaria		
high x_1	0.95 ± 0.22	1.19
x_2	0.94 ± 0.24	1.19
low y_1	0.27 ± 0.12	0.40
y_2	0.27 ± 0.12	0.40

[1]Based on actual stock concentrations and measured dilution flows.

the high test concentrations and about 30% less in the low test concentrations than in the mixing cells. Apparent degradation of phenolic compounds was greater at low test concentrations. This resulted in actual exposure concentrations that averaged 21-32% less than calculated (Table 2). MAKIMA (1977) found that a replacement time of 2.5 hr was sufficient to maintain test concentrations of highly degradable materials. However, the reduction in expected nominal concentrations occurred in our tests despite a relatively high volumetric turnover of about two solution exchanges per hour.

Variability in actual exposure concentrations may be attributed to dilutor design and could be reduced with greater flow adjustment effort and/or modifications in the dilutor apparatus. Volatility could also be a factor. Bacterial degradation of phenolic compounds throughout the dilutor system was apparent and is typical of long-term toxicity tests involving phenols (BUIKEMA et al. 1979). We noted heavy bacterial growth that had to be cleaned from outlet screens and drains daily after 8-10 days of testing.

Initial WSFs of SRC II contain a significantly higher concentration of total organic carbon (approximately 20-100X) than similarly derived mixes of crude and refined oils (GIDDINGS et al. 1980, STATES et al. 1980). This reflects the high concentrations of water-soluble phenolic compounds found in SRC II liquids. Due to relative solubility of the SRC II liquid we tested, toxic solutions can be generated with less mixing energy than is required to generate comparable toxicity of petroleum products. Because of the efficiency of extracting testable concentrations of WSF the size of the system is relatively small compared to those used for materials with lower water solubility (GINGERICH et al. 1979, VANDERHORST et al. 1977).

Consistency of extracted WSFs reduced the need for extensive, routine chemical monitoring and insured exposure of test organisms to constant toxicant levels. Our mix and separation system also saves considerable time by eliminating the need for batch-prepared mixes. The overall experimental design of our mixing unit need not be restricted to use with coal liquifaction products but may be applied to other toxic materials, including extracts of less soluble "weathered" materials. A mix system similar in concept was used to generate WSFs of chloroform, a highly insoluble material (our data).

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