Reduction in Surfactants by Irradiation

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Detergents have been determined to be some of the largest contributors to today's water pollution conditions. Yet pollution is not produced by the total chemical constituents but by certain specific chemical structures. Linear Alkylate Sulfonate (LAS) is used as a wetting agent in certain detergents because it creates an effective surface barrier at the water/air interface. This barrier not only hinders the diffusion of oxygen from the air into the water but also holds in any carbon dioxide produced within the water. The present study was designed to investigate the effect of ionizing radiation on Linear Alkylate Sulfonate to overcome the surface tension effect of detergents.

Gamma rays from Cobalt-60 were utilized as the ionizing radiation. This particular material was used because, when encapsulated, it possesses the property of being a pure gamma-ray emitter and has a half-life of 5.24 years.

Facilities and Calibration

The cobalt source used in this experiment is on loan to Florida Institute of Technology from the United States Army Corps of Engineers. It is housed under 23 feet of water in a facility designed by the General Electric Corporation. The source is composed of eight BNL-type strips each of which contains six dimesized disks of Cobalt-60 mounted in a thin strip of stainless steel. This strip is doubly encapsulated in stainless steel and is welded shut.

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The Cobalt-60 facilities at Florida Institute of Technology were calibrated by the use of a silicon solar cell dosimeter. This technique was utilized because of its range of accuracy and its ease of operation. At the beginning of this study, one configuration produced a dose rate of 16,438.4 rads-perminute at the point where the samples were exposed. The second configuration of the Cobalt-60 strips produced a radiation dose-rate of 366.7 rads-perminute at the same point.

Effects of Radiation on Water and Surfactants

ALLEN et al. (1961) reported that the passage of ionizing radiation through water results in the production of hydrated electrons by the photo-electric effect, the Compton effect, or pair production. Fast electrons, or beta particles, transfer energy to the water molecules at an average of 100 electron volts per interaction. Because the energy required to decompose a water molecule is only 29±3 electron volts per angstrom and because of a linear transfer rate of approximately 0.02 electron volts per angstrom, several molecules of water decompose within a radius of 10 to 20 angstroms from the exitation point.

SWORSKY (1953, 1954, 1955, 1964, 1965, 1966) extensively evaluated the effects of gamma radiation from Cobalt-60 in water. He proposed that the water excites with a half-life of between 10^{-9} and 10^{-10} seconds and goes through the following changes:

First, the water molecule is excited and breaks down by the formation of OH radicals

$$H_2O + \gamma \rightarrow H_2O* + e_{aq}^-$$

 $2H_2O* \rightarrow H_3O^+ + OH^- + 2e_{aq}^-$

Secondly, these principal reducing species, the hydrated electrons (e_{aq}), along with the OH radicals and H_3O radicals further propagate the water decay chains

$$20H^{-} \rightarrow H_{2}O_{2}$$
 $2H_{2}O^{*} \rightarrow H_{2} + H_{2}O_{2}$
 $H_{2}O^{*} \rightarrow H^{+} + OH + e_{aq}$
 $H_{2}O_{2} \rightarrow 2OH$
 $OH + H_{2}O_{2} \rightarrow H_{2}O + HO_{2}$
 $2HO_{2} \rightarrow H_{2}O_{2} + O_{2}$

The final result is the production of molecular oxygen, peroxide, hydrogen peroxide, and other strong oxidizing agents. Sworsky showed not only that the formation of these reducing agents is enhanced in an acid medium but also that the overall dissolved oxygen content within the fluid is increased by exposure to ionizing radiation.

It must be emphasized that these few equations do not completely explain the extremely complex interactions taking place, but they are meant to give a general feeling for a few of the major interactions.

There have been numerous studies performed to evaluate the possible use of radiation for treatment of waste waters. BALLENTINE et al. (1969) and ALEXANDER (1969) have worked in this area, but their work contains no information concerning the effect of radiation on surfactants. FLEISCHMAN and PRICE (1967), COHEN (1965), and UNIDYNAMICS CORPORATION (1963) have investigated the effect of radiation on surfactants, but the surfactants tested were Alkylate Benzene Sulfonates which have not been used since 1965. However, COMPTON et al. (1969) found that the radiation dose decreased the dissolved oxygen content.

FLEISCHMAN and PRICE (1967) and COHEN (1965) showed that the amount of breakdown due to the irradiation of the surfactants tested depended upon the dissolved oxygen in the exposed fluid. FLEISCHMAN and PRICE (1967) used sources delivering 1.41 x 10³ radsper-hour and reported a 98 percent reduction at 54,000 rads. COHEN (1965) used a 3,400 curie source of Cobalt-60 and reported a 99 percent reduction in the ABS at a total absorbed dose of 35,000 rads. UNI-DYNAMICS (1963) reported a 99 percent reduction at 90,000 rads. These different findings appear to be caused by the different surfactants used.

Test Procedures

Linear Alkylate Sulfonate was used as an additive to distilled water. Test samples were created in the laboratory with predetermined concentrations of LAS. These concentrations were determined by the MOORE-KOLBESON (1956) methyl green benzene extraction method developed at the Robert A. Taft Sanitary Engineering Center. This technique is a modification of the Evans-Jones methyl blue chloroform extraction technique that is a standard and universally accepted method. All samples were tested just prior to and immediately following irradiation.

The irradiation process was accomplished by completely filling 7 ml. B-D vacutainers with the solution and then lowering them to the center of the ring of Cobalt BNL strips. The dose absorbed by the solution was determined by the time of exposure. Immediately after withdrawing the samples from the radiation facility, they were again tested for their concentrations of LAS.

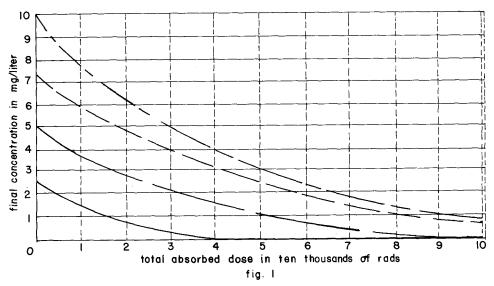
Because the possibility existed that the dose rate might be as effective as the total dose absorbed, samples were exposed under two different irradiation configurations. In the first configuration, the BNL strips were placed in a cylindrical structure with a diameter of approximately 12 inches. The solutions received irradiation at the dose rate of 16.438.4 radsper-minute. In the second configuration, the BNL strips were moved to the outer walls of the irradiator pool. Under these conditions, the solutions received energy at the dose rate of 366.7 rads-per-minute.

Results

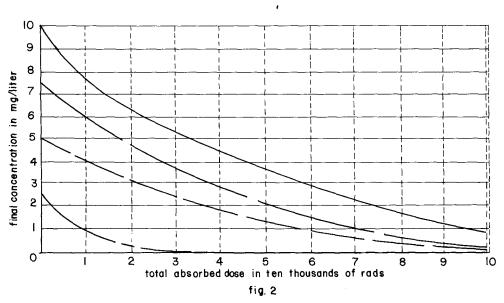
Over 200 aqueous samples containing LAS at concentrations of 2.5, 5.0, 7.5, and 10.0 mg/l were irradiated such that they absorbed 10, 20, 40, 60, 80, and 100 K rads of energy. Figures 1 and 2 show the mean reduction in concentration of the LAS as a function of irradiation dose. Figure 1 shows the effect at the 16.438.4 rad-per-minute rate of irradiation, while fig. 2 shows the effects of the 366.7 rad-per-minute rate of irradiation. This data indicates that the rate of irradiation is not nearly as important as the total absorbed energy. However, radiation can effectively reduce the concentration of LAS in aqueous solutions.

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Reduction in Surfactants with Irradiation dose rate of 16,438 rads/min



Reduction in Surfactants with Irradiation

dose rate of 3667 rads/min

REFERENCES

ALEXANDER, M. L.: M.S. Thesis, Purdue University (1969).

ALLEN, A. O.: The Radiation Chemistry of Water and Aqueous Solutions. New York: D. Van Nostrand Co., Inc. (1961).

BALLANTINE, D. S., et.al.: J. Wtr. Pol. Contr. Fed. 41, 3, part 1 (1969).

COHEN, J. B.: Ph.D. Dissertation, Cal. Inst. Tech. (1965).

COMPTON, D. M. J., S. J. BLACK, F. L. LIEURANCE, and W. L. WHITTEMORE: Gulf Feneral Atomic Report (August, 1969).

FLEISCHMAN, M. and R. H. PRICE: Env. Sci. Tech., 1, 7 (1967).

MOORE, W. A. and R. A. KOLBESON: Analytical Chem., 28, 2 (1956).

SWORSKI, T. J.: J. Chem. Phys., 21, 2 (1953).

SWORSKI, T. J.: J. Am. Chem. Soc., 76 (1954).

SWORSKI, T. J.: Rad. Res., 2, 1 (1955).

SWORSKI, T. J.: J. Am. Chem. Soc., 86 (1964).

SWORSKI, T. J.: Adv. Chem. Ser., Am. Chem. Soc, 50 (1965).

SWORSKI, T. J.: "The Precursor of Molecular Hydrogen," Notes from Oak Ridge National Laboratories (1966).

UNIDYNAMICS CORP.: Unidynamics Document No. D63-341 (Sept. 1963).