Effects of Gamma Radiation on Aqueous Solutions of Cyanide

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INTRODUCTION

Cyanide waste constitutes a major source of pollution from various industrial operations, especially from the electroplating process (TUWINER, 1973). There are at least 20,000 electroplating establishments in the United States, most of them involved with one or more cyanide plating operations. In such operations, the spent electroplating solutions and rinsing solutions are considered to be the principal cyanide waste solutions. Therefore, waste solutions containing cyanide ions must be disposed of in such a way as to meet desirable standards.

Disposal of such cyanide ions presents a very acute problem because of the toxicity of such solutions to animal and marine life. The threshold limit of toxicity, at infinite time, for fish has been reported to be 0.1 mg/l (DODGE, 1949). Activity of microorganisms responsible for self purification of water have been found to be greatly inhibited by concentrations of CN^- of at least 0.3 mg/l (LUDZACK, 1951).

Under Federal "Drinking Water Standards" for cyanide, the recommended maximum concentration is 0.01 mg/l, and 0.2 mg/l is considered the level of rejection. This standard has served as a guideline for the states and municipalities, most of which have adopted limits ranging from 0.05 to 1.0 mg/l (TERRY, 1962). Therefore, all cyanide wastes must be partially or completely decomposed before they may be discharged into natural streams or sewage systems.

In the past, the cyanides have usually been decomposed by purely chemical methods such as oxidation with chlorine (GURNHAM, 1965). Such methods, however, have proven to be rather troublesome in many respects, particularly in that a great deal of time is involved and there is a further health hazard introduced by the handling and disposal of chlorine.

MATERIALS AND METHODS

Irradiator

Gamma radiation from the Cobalt-60 source at Florida Institute of Technology was used for irradiating the solutions of cyanide. The facility, which is constructed of 4.67-foot thick concrete walls and ceiling, is built

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underground adjacent to the Crawford Science Building. Eight doubly encapsulated Cobalt-60 strips are located in a cylindrical container at the bottom of a twenty-four (24) foot deep water tank. All samples were lowered into the tank to the center of the cylindrical arrangement of Cobalt-60 strips. Thus all samples were evenly irradiated from all directions in a large aqueous environment.

Calibration of the radiation source was performed monthly by the use of a secondary standard solar cell. In December, 1974, the dose rate was 215 rads/sec (0.774 megarads per hour). The relation between exposure time and radiation dosage can be seen in Table I below:

TABLE I

EXPOSURE TIME REQUIRED FOR ABSORPTION OF RADIATION

Radiation Dosage	Exposure Time
10 KR	46.6 sec.
100 KR	7 min. 46.0 sec.
1,000 KR	1 hr. 17 min. 40.0 sec.
10,000 KR	12 hr. 56 min. 40.0 sec.

Where 1 KR is equal to 1,000 rads, one rad is equivalent to 6.2×10^{16} ev (electron volts) per liter of water, or the absorption of 100 ergs of energy per gram of material.

Experimental Procedure

A set of potassium cyanide (KCN) sample solutions were prepared by dissolving 2.51 grams of pure potassium cyanide in one liter of distilled water in order to make the solution containing 1,000 milligrams of cyanide ions per liter. The solution was then diluted to obtain concentrations of 100, 10, and 1 mg/l.

Samples were placed in 105 ml glass bottles with water-tight caps. They were lowered into and left in the center of the radiation field for a certain period so that they would absorb various amounts of energy ranging from 10 KR to 10,000 KR as was shown in Table I.

All samples were analyzed within less than one hour after they were removed from the radiation field. The remaining cyanide in the samples was analyzed by using the Pyridine-Pyrazalone Method an adoption of the Colorimetric method in Standard Methods (1971).

During this procedure, the colorless samples developed into a pink color, then turned to a blue color in a few minutes. In measuring the color of samples, the Spectronic-20 was used to read absorbance at 618 nm on all samples and standards and converted to cyanide concentrations.

RESULTS

Four independent sets of cyanide solutions were prepared with concentrations of approximately 1 mg/l, 10 mg/l, 100 mg/l, and 1,000 mg/l of cyanide ions One hundred and five (105) milliliter samples from each of the concentrations of cyanide for each of the independent prepared solutions were irradiation. The irradiation doses were 10 KR, 100 KR, 1,000 KR, and 10,000 KR.

Maximum, minimum and mean values of the cyanide remaining in the samples following each radiation dose were recorded for all samples of each concentration following each radiation dose. Standard deviations were determined for each mean value. Table 2 shows the results of these experiments. Figure 1 illustrates the percent reduction in the cyanide as a function of irradiation.

TABLE 2

EFFECTS OF IRRADIATION ON CYANIDE CONCENTRATION OVER FOUR (4) ORDERS OF MAGNITUDE

DOSAGE	NUMBER INDEPENDENT SAMPLES	MAXIMUM (mg/l)	MINIMUM (mg/l)	MEAN (mg/l)	STANDARD DEVIATION
0	6	1.56	0.81	1.17	0.31
10	6	1.20	0.50	0.75	0.27
100	6	0.96	0.31	0.56	0.28
1,000	6	0.35	0.18	0.24	0.07
10,000	6	0.08	0.03	0.05	0.02
0	6	12.80	9.60	11.30	1.44
10	6	12.00	8.10	10.12	1.58
100	6	9.20	3.20	5.88	2.29
1,000	6	3.20	0.50	1.37	1.03
10,000	6	0.50	0.04	0.17	0.17
0	6	156.00	99.00	118.50	23.28
10	6	140.00	89.00	106.00	20.39
100	6	134.00	70.00	89.30	23.69
1,000	6	72.00	21.00	48.00	21.42
10,000	6	6.00	3.00	4.50	1.22
0	6	1,620.00	1,050.00	1,322.00	247.90
10	6	1,560.00	850.00	1,133.00	256.66
100	6	1,480.00	840.00	1,042.00	229.21
1,000	6	820.00	330.00	640.00	164.49
10,000	6	21.00	12.00	14.50	4.18

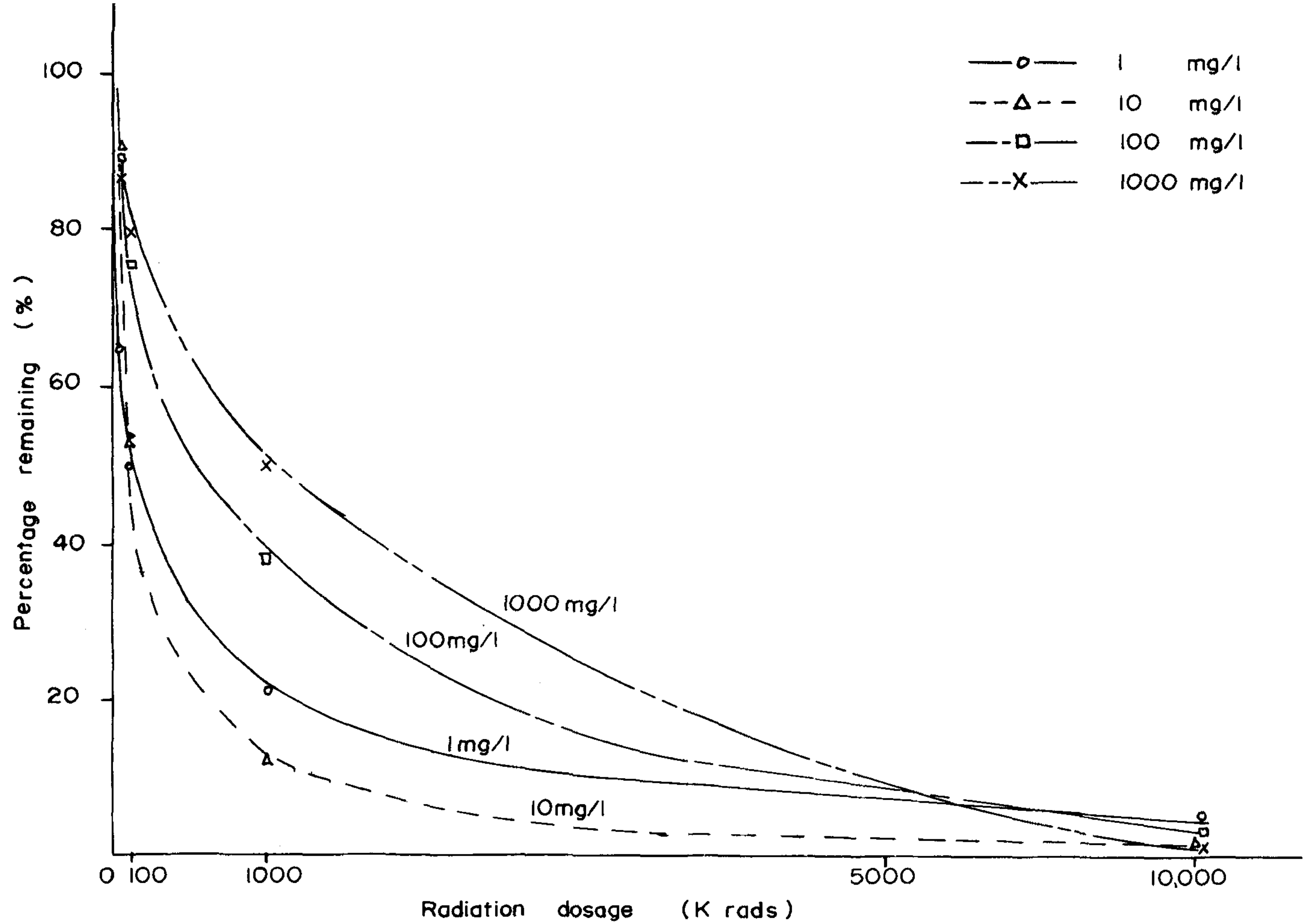

Fig. 1. Effects of irradiation on four concentration of cyanide.

A statistical analysis was performed to determine if the residual concentration of cyanide was more dependent on original concentration or on irradiation dosage absorbed by the solution. An analysis of variance (ANOVA) was applied to the data to determine these factors (HICKS, 1966). This method of statistical analysis is designed to handle situations in which the quantitative effects of particular variables are uncertain. Table 3 shows a Model I two-way analysis of variance where both factors are fixed treatment effects. The purpose of the analysis of variance is to estimate the true difference among the group means.

TABLE 3

ANALYSIS OF VARIANCE FOR CYANIDE REMAINING IN SAMPLES

SOURCE OF VARIATION	DEGREE OF FREEDOM	SUM OF SQUARE	MEAN SQUARE	F RATIO	SIGNIFICANT LEVEL
Radiation Dosage	3	45526.97	15175.66	272.01	1%
Concentration	3	2675.77	891.92	15.99	1%
Interaction	9	3335.82	370.65	6.64	1%
Error	80	4463.62	55.79		
Total	95	56002.18			

This table shows that the remaining concentration of cyanide is more dependent on the irradiation dosage than on the original concentration as indicated by the relative value of the F-ratio. However, the original concentration of cyanide is one of the determining factors as is shown by the F-ratio value of nearly 16.

Results of this experiment shows that gamma radiation can be effective in the removal of cyanide from aqueous solutions. However, the data shows that very large doses of irradiation are necessary for reductions in concentrations below 1 mg/l if the original concentration is above 10 mg/l. Thus, the utilization of gamma radiation for the reduction in cyanide from industrial waste will depend upon the discovery of a synergistic agent that can increase the effectiveness of the irradiation.

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