. . . . See Report 806-a (Copy) Original: Fish Division
cc: Education-Game

INSTITUTE FOR FISHERIES RESEARCH
DIVISION OF FISHERIES
MICHIGAN DEPARTMENT OF CONSERVATION
COOPERATING WITH THE
UNIVERSITY OF MICHIGAN

ALBERT S. HAZZARD, PH.D.
DIRECTOR

ADDRESS
UNIVERSITY MUSEUMS ANNEX
ANN ARBOR, MICHIGAN

August 19, 1942

REPORT NO. 806

A PROGRESS REPORT ON THE TOXICITY THRESHOLD EXPERIMENTS INDICATING THE EFFECTS ON FISH LIFE OF THE PRODUCTS DERIVED FROM THE POLYSULFIDE TREATMENT OF CYANIDE WASTES

Carl L. Hubbs and George N. Washburn

This report briefly summarizes the experimental work undertaken at the request of the Michigan Stream Control Commission, with the cooperation of Dr. B. H. Vollertsen of the E. I. duPont de Nemours Company (Niagara Falls, New York). The experiments are being continued. At a later date, when the experiments have been completed, a final report will cover the entire project in more detail.

The experimental work was conducted in the Experimental Aquarium of the University of Michigan. The water used in this experiment was the filtered, circulating aquarium-room water which has proven to be satisfactory for fish life. The experimental equipment consisted of wide-mouth two-quart jars, each equipped with an air line. Each concentration of the material tested was made up to one liter and two small fish were used in each trial run. Two general procedures were followed: one was to pre-aerate the solution 20 minutes before the fish were introduced and to continue the aeration as long as the fish remained alive; the other was to pre-aerate for 24 hours before the fish were introduced. The object of this long aeration was to oxidize the excess polysulfide in the solution. The free sulfur precipitated out, leaving a clear liquid which was decantered off and used in the experimental run. In this way, a rough estimate of the toxicity of the excess polysulfide could be determined. The time was noted when the fish were put in the solution and again recorded when the fish died. An arbitrary time of 96 hours was set as the duration for a trial run. If at the end of this time, the fish were still alive and in apparent good health, the run was concluded.

The computations of the concentrations used in these tests were based upon the analytical data furnished by B. H. Vollertsen. These analyses accompanied the shipment of the treated cyanide wastes.

EXPERIMENTAL RUN WITH THE BLUNTNOSE MINNOW HYBORHYNCHUS NOTATUS

A supply of adult bluntnose minnows was taken by seine from the York Pond, near Saline, Michigan. These fish were brought to the Aquarium and placed in stock tanks. Many were in the middle of their spawning season and consequently subject to fin rot. They did not hold well in the stock tank and the mortality rate was high. They were used as test fish on the sodium thiocyanate salt only and then were discontinued as the validity of the tests was doubted. It is hoped at a later date that a repeat test can be made with this species of fish. Below is a brief summary of the results of the tests conducted on the sodium thiocyanate salts:

Concentration of NaCNS in ppm. of solution.	Remarks
25,000 to 50,000	The fish died at these concentrations in from 2 to 5 minutes.
500 to 1,000	The fish lived from 9 to 32 hours.
50 to 90	The fish lived from 57 hours to end of run at 96 hours.
0 to 50	All of the fish lived to the 96 hour period and the test was terminated.

Interpretation of the above data

High concentrations of these salts are quickly lethal, while concentrations below 100 ppm. are only slightly toxic. Concentrations below 50 ppm. (equivalent to approximately 30 ppm. of NaCN) appear to be non-toxic for this fish. Tests with other fish did not indicate lethal effects in the 96-hour period, resulting from the use of concentrations lower than 500 ppm. Possibly the condition of the spawning fish interfered with the test.

EXPERIMENTAL RUN WITH THE CREEK CHUB, SEMOTILUS ATROMACULATUS

A very uniform stock of two- to three-inch fish was obtained from an experimental pond near Saline, Michigan. These fish were all of this year's hatch and were in apparent good health as during the experimental run not a single fish was lost in the holding tank. Below are the results obtained from the tests of the various materials:

SODIUM THIOCYANATE SALTS

These salts were the first of the products to be tested as this is the end product in the polysulfide treatment of NaCN, which was present in the other solutions.

Concentration in ppm. of NaCNS in solution	Remarks
800 to 1,000	The fish remained alive in these concentrations from 15 to 20 hours.
600 to 800	The fish remained alive in these concentrations from 65 to 81 hours.
00 to 600	All of the fish were alive at the end of 96 hours.

Interpretation of the above data

Concentrations of about 1,000 ppm. are definitely toxic and higher concentrations would no doubt be more quickly lethal. Concentrations below 600 ppm. (equivalent to 480 ppm. of NaCN) had no apparent effect upon the fish. It will be recalled that the toxicity threshold of NaCN as previously determined in this laboratory is less than 1 ppm.

COPPER PLATING SOLUTION

This solution originally contained 3,000 ppm. of NaCN, according to the information furnished with the sample; after treatment it tested 6 ppm. of NaCN and 5,000 ppm. of NaCNS. Just before the experimental work was begun a test by Arnold Heine revealed no free NaCN.

ppm. of NaCNS in solution	Equivalent to ppm. of NaCN before treatment	Time the fish remained alive in the solution	
		Normal aeration	Pre-aeration
2,500	1,500	1 minute	(no test)
500	300	2 to 2 1/2 min.	(no test)
250	150	2 to 2 1/2 min.	2 to 5 hours
125	75	(no test)	4 to 6 hours
90	54	(no test)	30 hours
80	48	(no test)	60 to 72 hours
75	45	(no test)	alive at 96 hours
50	30	5 to 22 min.	alive at 96 hours
9	5.4	2 to 96 hours	alive at 96 hours
0 to 8.5	0 to 5.1	alive at 96 hours	alive at 96 hours

Interpretation of the above data

The toxicity threshold for the normally aerated solution was 8.5 ppm. of NaCNS and for the pre-aerated solution 75 ppm. A difference of 66.5 between the two thresholds can be attributed to the toxicity of the excess

polysulfide, or some other substance which can be denaturized or removed by prolonged aeration. The toxicity in terms of NaCNS was much higher than indicated in the preceding test. If the analyses furnished are correct, and the tests adequate, some other toxic materials must be present in this solution. More experimental work should be done before any definite conclusions are drawn. For the normally aerated solution, the dilutions would be 1 part of stock solution to 588 parts of water to attain the 8.5 ppm. of NaCNS. For the pre-aerated solution, the dilutions would be 1 part of the stock solution to 66 parts of water to make up to 75 ppm. of NaCNS.

CARBURIZING SALTS SOLUTION

According to the analysis furnished with the sample, this solution originally contained 9,000 ppm. of NaCN, and after treatment with polysulfide tested 8 ppm. of NaCN and 11,000 ppm. of NaCNS. A test by Arnold Heine made just before the experimental work was begun revealed no free NaCN.

ppm. of NaCNS in solution	Equivalent to ppm. of NaCN before treatment	Time fish remained alive in solution	
		Normal aeration	Pre-aeration
5,500	4,500	2 to 3 min.	(no test)
1,100	900	3 to 4 min.	(no test)
880	720	(no test)	approx. 47 hours
550	450	3 to 4 min.	67 to 84 hours
495	405	(no test)	alive at 96 hours
165	135	5 to 6 hours	alive at 96 hours
77	63	approx. 56 hours	alive at 96 hours
0 to 71.5	0 to 58.5	alive at 96 hours	alive at 96 hours

Interpretation of the above data

The difference in ppm. of NaCNS between the two thresholds established is 423.5. This is probably due to the excess polysulfide present in the normally aerated solution. Though the pre-aerated solution threshold did not quite reach the 600 ppm. of NaCNS previously established, a longer aeration period may achieve this goal. The toxicity threshold of the normally aerated solution was approximately established by a dilution of 1 part of stock solution to 153 parts of water; that of the pre-aerated solution, 1 part of stock solution to 22 parts of water.

SODIUM CYANIDE SOLUTION

This solution was analyzed as containing 42,000 ppm. of NaCN before treatment, and 2 ppm. of NaCN and 50,000 ppm. of NaCNS after treatment. A test just before experiments were conducted revealed no free NaCN.

ppm. of NaCNS in solution	Equivalent to ppm. of NaCN before treatment	Time fish remained alive in solution	
		Normal aeration	Pre-aeration
25,000	21,000	not over 2 min.	(no test)
2,500	2,100	not over 4 min.	(no test)
1,000	840	(no test)	48 to 83 min.
650	546	(no test)	81 to 96 hours
600	504	(no test)	alive at 96 hrs.
500	420	5 to 7 minutes	alive at 96 hrs.
450	378	4 to 6 hours	alive at 96 hrs.
440	369.6	44 to 96 hours	alive at 96 hrs.
0 to 420	0 to 352.8	alive at 96 hours	alive at 96 hrs.

Interpretation of the above data

The difference in ppm. of NaCNS between the two thresholds established is 180. The difference is not as great in this solution as in the others and probably the excess polysulfide was completely oxidized by the aeration. For the pre-aerated solution, the threshold previously established with the NaCNS salts was verified. The dilutions necessary to reach the toxicity thresholds found for this solution are: 1 part of stock solution to approximately 119 parts of water for the normally aerated solution, and 1 part of stock solution to about 83 parts of water, for the pre-aerated solution.

EXPERIMENTAL RUN WITH THE PUMPKINSEED SUNFISH, LEPOMIS GIBBOSUS

These fish were taken from the Huron River near Ann Arbor, Michigan. The average length was 2 to 3 inches. The same procedure was used with these fish as with the others. These tests are not completed, but the thresholds found are about the same as for the creek chub.

The threshold established for the sodium thiocyanate salts was 500 ppm. of NaCNS.

That for the copper plating solution, with normal aeration, 15 ppm. of NaCNS.

The tests with the pre-aerated copper plating solution is not completed.

The threshold established for the normally aerated carburizing salts solution was 77 ppm. of NaCNS. The corresponding pre-aeration test is not completed. The threshold established for the sodium cyanide solution, with normal aeration was 200 ppm. of NaCNS.

PRELIMINARY CONCLUSIONS

(1) The polysulfide treatment, changing NaCN into NaCNS, greatly reduced the toxicity of cyanide wastes.

(2) Considerable further decrease in the toxicity of the effluents could be accomplished by the destruction of the excess polysulfide which seems to be required for the completion of the reaction. In our experiments this was accomplished by prolonged aeration (the sulfur precipitating out). Perhaps a spray system would be effective.

It is thought probable that the toxicity of the polysulfide was due to its combining with the dissolved oxygen. The fish showed symptoms of asphyxiation. Tests for D.O. by the "Standard Methods" were attempted, but could not be completed on account of the polysulfide present. A qualitative test indicated that some dissolved oxygen was present, but whether in quantity sufficient for fish life was not learned.

(3) The treated copper-plating solution appeared to have a higher toxicity, that could not be explained in terms of the NaCNS present. Prolonged aeration again greatly reduced the toxicity but not nearly to the point attained with the other materials; therefore the other toxic substance seemingly present was probably not excess polysulfide. It is thought likely that copper is involved. Our cooperating chemist (Arnold Heine) has not been able to make a test, either quantitative or qualitative, for the copper in this solution.

SUGGESTIONS

(1) The tests should be continued, with some repetition for verification.

(2) Further consideration should be given to the special toxicity of the treated copper-plating solution. Information is needed on the amount of copper present and on the form in which it is combined. If any other potentially toxic substances are present in this solution, that are lacking in the others, this information too should be at hand. Could the polysulfide in the presence of copper, or some compound derived from the polysulfide in this treatment, be rendered resistant to oxidation by bubbling air?

(3) It is considered desirable that toxicity tests be run with dilutions of the actual effluent from a plant using the polysulfide treatment of cyanide wastes.

INSTITUTE FOR FISHERIES RESEARCH

Experiments run from June 24 to present, by George N. Washburn with cooperation of John T. Greenbank.

Report prepared August 19, 1942, by Carl L. Hubbs and George N. Washburn.

Original typed by Maxine Weitzel (Dr. Hubbs' secretary); copy typed by V. Andres.

Copies furnished: A. S. Hazzard (Institute for Fisheries Research)
Dr. B. H. Vollertsen (E. I. duPont de Nemours Co.)
Milton P. Adams (Stream Control Commission)