THE TREATMENT OF CYANIDE WASTE WITH LIME-SULPHUR TO DESTROY ITS TOXICITY

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STATEMENT OF THE PROBLEM

The primary objective of this study is to determine the feasibility of the use of lime-sulphur in the treatment of cyanide waste to destroy the toxicity or lethal effect of this industrial sewage as it presents itself in the manufacture of case hardened steels and in electro-plating processes.

It is the writer's belief that a more satisfactory method of treatment of this waste can be found. The present methods of treatment present problems which constitute a hazard either to the safety of individuals or from some other standpoint.

SURVEY OF THE LITERATURE

Various salts of cyanide, chiefly sodium and potassium, are used in the electro-plating industries for the plating of copper, zinc, nickle, chromium and other metals. The washings from these plated parts manufactured for every day needs contain cyanides in varying concentrations and, hence, create a problem of disposal in a safe and satisfactory manner.

Cyanides are very poisonous and when discharged into streams as a method of disposal create a menace not only to fish and other aquatic life, but to cattle and other animals which may frequent the stream. Also there is always the possibility of humans' coming in contact with a stream so polluted.

The Toxic Action of Cyanides

The toxic action of the cyanides is exerted physiologically to reduce or entirely eliminate the utilization of oxygen.[1]

This may be presented better by observing Professor Andrews Karsten's, of South Dakota State School of Mines, experiments on the effects of cyanide on trout.[2] He states that he believes the action of the cyanide was through the blood by the formation of cyano-hemoglobin and points out that perhaps the hemoglobin has a marked affinity for cyanide. Hence, the blood carried cyanide rather than oxygen to parts of the body which require oxygen. He observed that fish killed by cyanide had extremely red gills.

Medical handbooks bear[3] out his theory. The central nervous system is first stimulated and then depressed and finally paralyzed. The stimulation is especially marked in the medulla, so that the respiratory center, vasomotor, vagal centers are stimulated, resulting in an acceleration of the respiration, constriction of the blood vessels, and slowing of the heart. The blood pressure rises on account of vasoconstriction in spite of the slowing of the heart, but soon falls on account of vasodilation. The respirations are at first accelerated as stated before, but soon become slowed and shallow. Coma follows quickly, sometimes preceded by convulsions; death being due to asphyxia. Hydrocyanic acid enters the blood very rapidly and, while in the circulation, profoundly affects metabolism so that the tissues lose their power of absorbing oxygen. Contrary to previous belief it does not fix oxygen more firmly to the hemoglobin, but forms cyanohemoglobin which differs from ordinary hemoglobin in its bright red color, and which is responsible for the bright red color of the blood.

M. M. Ellis[4] of the United States Department of Commerce, Bureau of Fisheries, reported in his work that

1. Ammonium ferrocyanide of 150-200 p.p.m. killed orange spotted sunfish in one hour.
2. Ammonium thiocyanate 200 p.p.m. was lethal to fish.
3. Potassium cyanide of 0.1 to 0.3 p.p.m. in hard water killed gold fish in 3-4 days.
4. Potassium ferricyanide of 2000 p.p.m. was not lethal to minnows and gold fish.
5. Potassium ferrocyanide of 2000 p.p.m. was not lethal to minnows and gold fish.

Washings from plating rooms will vary as to the type of plating process and as to the management of the plant, but in general they will run between 300-500 p.p.m. of cyanide. Care should be taken that no vats are dumped during the process of cleaning, but rather that the contents should be transferred to another vat or tank. With good cooperation of the employees there is no reason why concentrated cyanide should enter any sewer or stream.

Disposal by Dilution

Present methods of disposal of cyanide waste are, in the writer's opinion, none too satisfactory. Dilution by discharge into streams is an easy method of disposal, however, great care should be taken that the dilution is sufficient to reduce the cyanide content below that lethal to fish and other aquatic life. For average plating room waste this should be about one part in two to three million. Care should be taken to introduce the waste evenly over the stream so that areas of high concentration of cyanide do not pass down stream. At best this is a poor method of disposal and should be resorted to only in cases of accident when no other method can be used.

Ponding of the Waste

Ponding the waste is a frequent practice of many factories. The ponds are made by throwing up an earth dyke about an area of land forming a retention basis for the waste. It is good practice to fence these ponds in and put up warning signs to the public. The use of ponds is unsatisfactory in that wells in the vicinity may become contaminated by seepage or children may come in direct contact with the waste. The cyanide content of waste treated in this manner will entirely disappear over a period of time if no new waste is added. Several factors effect the rate of reduction of the cyanide. Rain or dilation, seepage, temperature and chemical action with the elements all tend to aid this cause. No definite time limit can be placed as to complete removal of the toxic substances since the above mentioned factors all enter into the destruction of the cyanide. Before a pond of waste is drained, selected samples should be collected and tested for cyanide. While this method of treatment is rated as a better means of cyanide waste disposal than discharge direct to the stream, it is none too good and should be resorted to only in case other methods are not available.

Reactions of Cyanides

Listed below are some reactions of the cyanides and perhaps explain the elimination of cyanides by ponding.(1)

An aqueous solution of the cyanides is unstable and hydrolysis takes place with the production of ammonia, thus:

$$KCN + H_2O \longrightarrow HCOOK + NH_3$$

The cyanides are oxidized by oxygen of the air and cyanates are produced. These in turn are hydrolized in water solution to produce ammonia and an acid carbonate.

$$KOCN + H_2O \longrightarrow NH_3 + KHCO_3$$

The cyanides are decomposed by carbon dioxide with the production of HCN a soluble and volatile gas which is gradually evolved in air.

$$KCN + H_2CO_3 \longrightarrow HCN + KHCO_3$$

Acid Treatment

Two recent methods developed in the last ten years have proved quite successful in the destruction and removal of the cyanide in plating room waste.

When cyanides come in contact with acids, hydrogen cyanide or hydrocyamic acid is formed which is extremely volatile and can be removed from the waste by bubbling air through the waste. The success of the treatment depends on the acid concentration required, the period of aeration, the completeness of cyanide removal and the toxicity of the remaining waste.

In this process the plating room wastes are collected in an acid resisting tank and the correct amount of sulphuric acid in excess of 10% based on the p.p.m. potassium cyanide and alkalinity of solution is added. The contents of the tank are aerated for ten to sixteen hours, depending on the concentration of potassium cyanide, to remove the hydrocyanic acid gas. Important factors to watch in this treatment as observed by E. F. Eldridge[1] are as follows:

1. In calculating the correct amount of acid to use for neutralizing the potassium cyanide, the natural alkalinity of the water must be neutralized. Hence a test to determine the alkalinity in terms of calcium carbonate must be run and the necessary amount of sulphuric acid to react with it is calculated and added to amount necessary for the potassium cyanide treatment.
2. Experiments have shown that 10% more acid should be used than is theoretically needed in the reaction to obtain best results.
3. The pH of the solution during treatment should never be higher than between 5 and 6 and may be lower for complete removal of the cyanides.
4. About 7.5 cubic feet of air is required per gallon of waste treated and should be admitted to solution through diffuser plates placed in bottom of the tank. They should have an area of about one quarter of the area of the tank.
5. A stack of not less than 40 feet in height and an air-tight hood should be attached to the top of the tank through which a forced air fan blows the hydrocyanic acid gas into the air. The gas is very toxic to humans and utmost care should be observed at all times to handle this method of treatment in a safe way. It is this reason alone (safety) that marks this type of treatment as being not too satisfactory.

Potassium Permanganate Treatment

Oxidation of the cyanides with potassium permanganate[1] is the other method of more recent treatment. This reaction will occur in either a neutral or alkaline solution and is as follows:

$$3KCN + 2KMnO_4 + 3H_2O \longrightarrow 2Mn(OH)_4 + 5KOCN$$

Sufficient time must be allowed for the complete reaction to take place; usually twelve to sixteen hours are necessary. By equation 1.62 parts by weight of $KMnO_4$ are required to exactly oxidize the one part of KCN or its equivalent.

In this process, as in the latter, the wastes are drawn to a holding tank which should be equipped with a sludge hopper and drawn-off valve. They are treated with the calculated quantity of $KMnO_4$. Thorough mixing for about thirty minutes by use of diffused air plates followed with a settling period of fifteen hours completes the treatment. At the end of this period the clear supernatant liquid should be diluted one to one and then may be drained to the sewer or to the stream. The sludge, although not toxic in concentrations between 600 to 1000 p.p.m., will kill fish above that. Hence it probably would be best to build a small sludge drying bed for sludge disposal although small amounts of the sludge added to a stream with a liberal flow would probably not cause any trouble.

A study on the treatment of 10,000 gallons of cyanide waste of 100 p.p.m. was made to determine the cost of the above methods. Using the acid treatment, the cost was \$2.04, and using $KMnO_4$, the cost was \$2.15. This included treatment of the alkalinity of the water and aerating cost.

A further study by Eldridge[1] proved conclusively that the addition of cyanide to sewage sludge greatly inhibits its digestion, hence eliminating the possible use of municipal sewage treatment plants as a satisfactory method of disposal of cyanide waste.

EXPERIMENTAL WORK

The aim of this work was to determine whether or not if potassium cyanide were treated with a solution of lime-sulphur the toxic effects of the cyanide would be destroyed.

Potassium cyanide, used, was obtained from the Olds Motor Works and contained 96% KCN by analysis. The commercial lime-sulphur purchased from Carrier-Stephens Chemical Co. showed an analysis as follows:

Baume - 32° at 15°C.

Sulphur - 24%

Calcium polysulphide - 30.0%

Calcium thiosulphate - 1.5%

Water and other inert ingredients - 68.5%

Lime and sulphur in solution - 31.5%

One of the first problems presenting itself in this work was the method of testing or checking the results of treatment. The first method used was a colorimetric test as follows:

<u>Determination of Cyanides in Water</u>

Solutions:

(1) Acetone containing 4 grams of free sulphur per 100 cc.

(2) Concentrated nitric acid.

(3) Ferric nitrate solution containing 5 grams ferric nitrate per 100 cc.

(4) Permanent color standards from potassium chloroplatinate (a) and cobaltus chloride (b).

(a) Dissolve 0.4 gram of potassium chloroplatinate in a small amount of water, add 20 cc concentrated HCl and dilute to exactly 100 cc with distilled water.

(b) Dissolve 4.8 grams cobaltus chloride ($CoCl_2 .6H_2O$) in a small amount of distilled water, add 20 cc of concentrated HCl and make up to exactly 100 cc.

Add the exact amounts of (a) and (b) as given in the following table to 100cc. Nessler tubes and make up to the mark.

CN p.p.m.	(a) cc	(b) cc
0.5	4.5	1.0
1.0	6.0	1.6
2.0	12.5	3.8
3.0	15.2	6.0
4.0	24.5	10.0
5.0	38.0	12.5

Procedure:

(1) To about 110 cc of the sample to be tested in a beaker add 2cc of the acetone and sulphur mixture. (Be sure to shake the mixture thoroughly so that the sulfur is well mixed with the acetone before adding it to the sample. Then add it quickly before the sulfur has time to settle.)

(2) Heat the solution to boiling. Boil gently until cloudiness disappears. Should the cloudiness reappear upon cooling, heat until it does disappear permanently.

(3) When cool, add 1 cc of concentrated nitric acid and 3 cc of ferric nitrate solution.

(4) Filter into a Nessler tube to the 100 cc mark and compare the color with the permanent standards prepared above.

This test failed to check results because it depends upon the combination of the free sulphur with KCN to form potassium thiocyanate. Upon addition of $Fe(NO_3)_3$, it forms ferric thiocyanate which gives the characteristic red color. However, in the treatment with lime-sulphur this reaction has already taken place and the red coloration is obtained even though no cyanide as such is present.

The standard silver nitrate test was next attempted. Complete procedure for this test may be found on page 14 of "Analysis of Water and Sewage" by Theroux, Eldridge and Mallmann. This test is given for chlorides but may be used for cyanides as well. The test also failed because a silver sulphide precipitate is formed from the excess lime-sulphur and interferes with the test.

Since chemical tests cannot be used, it was decided at this time to use goldfish as a check on the treatment by placing them in treated solutions to determine if the toxicity had been destroyed. All tests completed in the laboratory were checked by gold fish and the table which follows shows the collected data:

TABLE NO. 1

Fish Test with Treated Cyanide Solution

No. of Test	Concentration of KCN	c.c. used	Dilution of Lime-sulphur	Amount used	Time of fish to die in minutes
1	- -	- -	.01 of 1%	1000cc	57
2	- -	- -	.01 of 1%	1000cc	1495
3	10.2 p.p.m.	1000cc	none	none	Died during night
4	10.2 p.p.m.	1000cc	.01 of 1%	25cc	" " "
5	10.2 p.p.m.	1000cc	.01 of 1%	50cc	1500, apparently OK
6	10.2 p.p.m.	1000cc	.01 of 1%	50cc	Died after 24 hrs.
7	10.2 p.p.m.	1000cc	.01 of 1%	150cc	Died after 48 hrs.
8	100.0 p.p.m.	1000cc	.1 of 1%	none	45
9	100.0 p.p.m.	1000cc	.1 of 1%	25cc	80
10	100.0 p.p.m.	1000cc	.1 of 1%	50cc	90
11	100.0 p.p.m.	1000cc	.1 of 1%	75cc	105
12	100.0 p.p.m.	1000cc	.1 of 1%	none	90
13	100.0 p.p.m.	1000cc	.1 of 1%	- -	110
14	100.0 p.p.m.	1000cc	.1 of 1%	- -	115
15	100.0 p.p.m.	1000cc	.1 of 1%	75cc	65
16	100.0 p.p.m.	1000cc	.1 of 1%	100cc	65
17	100.0 p.p.m.	1000cc	.1 of 1%	125cc	65
18	100.0 p.p.m.	1000cc	.1 of 1%	150cc	65
19	100.0 p.p.m.	1000cc	.01 of 1%	50cc	20
20	100.0 p.p.m.	1000cc	.01 of 1%	100cc	15
21	100.0 p.p.m.	1000cc	.01 of 1%	150cc	15

Test number one was a blank test run on a .01% of lime-sulphur solution to determine if it were toxic itself to fish life. The dilution was made from distilled water because tap water causes precipitation of sulphur. This gold fish lived 57 minutes in this solution, however, death was undoubtedly due to lack of dissolved oxygen in the solution. Test number two follows exactly the same steps as number one except that the solution was aerated. In this solution the gold fish lived 25 hours with no ill effects. Temperatures of the aquarium and lime-sulphur solution were checked and found to be 66°F and 65°F, respectively. This was done to prevent any shock to the gold fish upon being transferred from one solution to another. At the end of this test a very fine light-colored, brownish precipitate had formed. A small amount collected in a test tube and treated with standard silver nitrate gave a heavy brownish black precipitate indicating that some form of a sulphide had been produced, possibly calcium sulphide.

Tests numbers 3, 4, and 5 were run as follows: Test number 3 contained one liter of 10.2 p.p.m. of KCN. No lime-sulphur solution was added. The solution was aerated from the beginning of the experiment (10:00 a.m.) for five hours. The gold fish was apparently in good shape at 6:00 p.m.; however, it died during the night. Test number 4 contained one liter of 10.2 p.p.m. of KCN and was treated with 25cc of 0.01% lime-sulphur solution. Air was likewise bubbled through this solution for five hours. The gold fish also was in apparent good health at 6:00 p.m. but died during the night. Test number 5 contained one liter of 10.2 p.p.m. KCN and was treated with 50cc of 0.01% lime-sulphur solution. This mixture was aerated for five hours as in tests 3 and 4. This gold fish lived for 25 hours or 1500 minutes and exhibited no ill effects from the treatment, hence was assumed to be in good health. However, 24 hours later this gold fish which had been placed in fresh aerated tap water was dead.

It may be well to explain here that all solutions of both lime-sulphur and potassium cyanide were made from distilled water. Aeration employed was for the purpose of building up the dissolved oxygen supply in the solution.

Tests numbers 6 and 7 were run to check the results found in number 5. Test number 6 contained one liter of 10.2 p.p.m. KCN and 50cc of lime-sulphur solution. The gold fish in this solution died between 36 and 48 hours after start of the treatment. Aeration was continuous. Test number 7 contained one liter of 10.2 p.p.m. KCN and 150 cc of .01 of 1% lime-sulphur solution and was continuously aerated. The gold fish lived in this solution between 48 and 60 hours. This check indicated possibilities of treatment even though the fish had died, perhaps due to some other outside factor which was not under control.

With this thought in mind from past results a further check was desirous. Hence, new solutions of potassium cyanide were made up of 100 p.p.m. concentration. It was believed that since the KCN concentration had been made ten times stronger that likewise the concentration of the lime-sulphur solution should be increased to 0.1%.

Test number 8 contained one liter of 100 p.p.m. KCN solution and was run as a blank. The gold fish lived 45 minutes. Test number 9 contained one liter of 100 p.p.m. KCN and 25cc of 0.1 of 1% lime-sulphur solution. The gold fish lived 80 min. in this solution. Test number 10 contained one liter of 100 p.p.m. KCN and 50cc of 0.1 of 1% lime-sulphur solution. The gold fish lived 90 minutes in this solution. Test number 11 contained one liter 100 p.p.m. KCN and 75 cc of 0.1 of 1% lime-sulphur solution

The gold fish lived 105 minutes in this solution. The last four fish, 8, 9, 10 and 11 were all aerated continuously until the fish had died. Although the fish lived over an hour in these solutions as treated, they all exhibited very marked evidences of the toxicity of the solution. About one-half hour after being placed in these treated synthetic wastes, the gold fish raced around in the tank, coming to the surface, often gulping air and even jumping from the water. They seemed to lack a sense of balance and were often observed swimming on their sides or back. In about 15 or 20 minutes more the fish had quieted down considerably, becoming very lackadaisical. The fish seemed to lack strength to swim and often sank to the bottom. The gills became very red and a reddish band had developed completely around the body of the gold fish at the point where the gills are attached to the body.

Tests number 12, 13 and 14 were run with the previous solutions used in tests number 9, 10, and 11. No additional treatment was used except to aerate the solution continuously. These three experiments were run to check the possibilities of a delayed effect of treatment. Results from these tests were as follows: The fish in test 12 died in 90 minutes, in number 13, 110 minutes and in number 14, 115 minutes. This seems to prove beyond any doubt that there was no delayed action.

To check further with these higher concentrations of both potassium cyanide and lime-sulphur solutions, a series of four more tests were run with increased amounts of lime-sulphur solution of 0.1% added. Test number 15 contained one liter of 100 p.p.m. KCN and 75cc of 0.1% lime-sulphur solution. Test number 16 contained one liter of 100 p.p.m. KCN and 100 cc of

0.1% lime-sulphur solution. Test number 17 contained one liter of 100 p.p.m. KCN and 125cc of 0.1% lime-sulphur solution. Test number 18 contained one liter of 100 p.p.m. of KCN and 150 cc of 0.1% lime-sulphur. All solutions were aerated continuously until the death of the gold fish. All the fish died within 65 minutes after starting the experiment. In this series of tests, as before, the gold fish acted very excited and swam about considerably, and then after a few minutes became very quiet with the characteristic deep red colored gills. In these increased doses of lime-sulphur, the treated mixture of potassium cyanide became quite cloudy and seemed to contain a very fine colloidal precipitate. This may have aided in bringing the life of the gold fish to a more rapid end, as this fine material could possibly have clogged the gills.

A final set of three tests was made with a higher dilution of lime-sulphur. Test number 19 was prepared by mixing one liter of 100 p.p.m. of KCN and 50cc of .01% lime-sulphur together. The solution was aerated continuously. The gold fish lived in this solution 20 minutes. Test number 20 was prepared by mixing one liter of 100 p.p.m. KCN with 100 cc of .01% lime-sulphur solution. The solution was aerated continuously and the fish died in 15 minutes. Test number 21 was prepared by mixing one liter of 100 p.p.m. KCN with 150 cc of .01% lime-sulphur solution. This was also aerated continuously and the fish died in 15 minutes.

INTERPRETATION OF RESULTS

In lower dilutions of both potassium cyanide and lime-sulphur, the experiments were more successful, however, outside physical or chemical factors may have caused this difference.

With the higher concentrations, the results were very unfavorable. The action of the gold fish indicated that the treatment was not satisfactory. Their reactions to the lethal effects of the treated cyanide waste proved quite conclusively that they were suffering from lack of oxygen. This was due to the toxic effects of the cyanide. The physiological action of the fish was exactly that of a cyanide poisoning as described in medical handbooks. Their reactions are first stimulated and later depressed until finally death occurs due to asphyxia. The fish had extremely red gills which was likewise a sign of cyanide poisoning.

SUMMARY OF EXPERIMENTAL RESULTS AND CONCLUSIONS

From the results of the experimental test run, it appears that the lime-sulphur lacked the ability to convert the cyanide to a cyanate or some other cyanide compound which is stable and much less or not at all toxic to fish life. This fact was shown more conclusively in the stronger concentrations of potassium cyanide. However, there is some chemical reaction which occurs when KCN and lime-sulphur are mixed together. A concentrated solution of KCN mixed with a small amount of lime-sulphur quickly formed a yellow colored precipitate which may have been free sulphur.

It is the writer's opinion that further study is warranted of this treatment by persons having more time as well as a better understanding of the chemistry involved. Having been called to active duty in the army cut short the experimental work of this thesis.

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