AN EXPERIMENTAL STUDY OF THE TREATMENT OF CYANIDE SOLUTIONS WITH LIME-SULPHUR TO DESTROY ITS TOXICITY

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An Experimental Study of the Treatment of Cyanide Solutions with Lime-Sulphur to Destroy Its Toxicity

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STATEMENT OF THE PROBLEM

The primary purpose of this experiment is to determine the possibility of using a lime-sulphur solution in the treatment of cyanide wastes to remove the toxic effect of the cyanide solutions. The cyanide waste is one of the most important from the standpoint of polution. There are few industrial wastes which are more hazardous. Many of the solutions used for cleaning and plating in industrial plants contain some form of the metallic cyanides. The disposal of these wastes is often difficult and dangerous. At present there is not an entirely satisfactory method of treatment as all methods are unacceptable for one or more reasons.

The precipitation of cyanide to lower toxic forms with the use of potassium permanganate is used to some extent by some plants, but the method is limited due to the expense involved.

The disposition of cyanide wastes by the acid reduction method is used by some plants. The deposit on, of evolved gases is a very serious problem, especially in crowded and built up areas.

Therefore a new method is being sought which will solve some of the problems encountered by the above two methods of handling cyanide wastes. The use of lime-sulphur has been suggested as the possibility of being a new method which will solve problems encountered by other methods of cyanide waste treatment.

SURVEY OF THE LITERATURE

Cyanide wastes may be found in every industrial plant in the country. Automobile factories and other industrial plants have plating rooms in which iron and steel parts are covered with coatings of copper, nickle, chromium and other metals. There are also the case hardening departments which use cyanides to a great extent. In the operation of plating rooms the different parts are suspended in vats containing the cleaning or plating solutions. When the particular operation is complete the parts are removed from the bath and rinsed in a vat of water. During the removing and the transfering of the parts from the cyanide vats to the rinse water, there are drippings which fall to the floor and are washed down the sewers. Also parts which are not regular, carry over varying amounts of concentrated cyanide solutions to the rinsing baths. This tends to keep the concentration of the cyanides up around 400 to 500p.p.m.. The lowest average a plant will have will be around 100 p.p.m. and the wastes from hardening rooms will run up to very high concentrations of around 20,000 p.p.m.. The wash water vats usually have a continuous flow of water through them so that this tends to keep the cyanide concentrations lower.

The cyanides are very poisonous and their discharge into streams is a constant menace to fish and aquatic life. Animal life which has access to such streams, where cyanide wastes may be, is also menaced. If such streams or ponds are not protected, children as well as adults may be killed by coming into contact with water containing cyanides.

The physiological action of cyanide is very important and can be explained better by referring to almost any medical book. If the acid, gas, or solid form of cyanide is delt with, care must be taken. Solutions of hydrocyanic acid applied to the skin will cause numbness and a partial loss of sensation. If cyanide is taken internally the central nervous system is at first stimulated and then depressed and finally paralysed. 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 the 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 becomes 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, a nd which is responsible for the bright red color of the blood. Eyes will become dilated and unconsciousness comes rapidly with convulsions. If a person comes incontact with cyanide gas, death is sure to follow, if they get a good dose in about 5-30 minutes.

Because of the nature of the wastes there are several important things to remember:

1. There should be complete safety to operators handling the disposition.
2. The wastes materials cannot be left in dumps or placed where contamination is a possibility.
3. In the handling of the deposition of cyanide wastes, at least two people should work together as a safety precaution.

Dr. M. M. Ellis of the United States Bureau of Fisheries makes the following statement about the toxic action of cyanides. "The simple cyanides exert a toxic action on living organisms by reducing or eliminating the utilization of oxygen. As a result of this physiological action, cyanide compounds reduce oxygen consumption and develop symptoms simulating asphyxia."

Professor Karstens' report on the physical effect of cyanide on fish was one of the first complete reports to be published. The trout, used in the experiment, were observed by Professor Karsten to die in rather an unusual manner. They indicated in their actions, efforts typical of trying to get out of the water. They showed all the evidence of suffering from the lack of air. Also a physical effect, which was noticed, was that the gills of the trout assumed a brilliant red color. This indicated that the action of the cyanide was likely through the medium of the blood by the formation of cyano-hemoglobin. This shows that the fish did not die from the lack of oxygen but were effected as humans are to a certain extent. The effect of cyanide on humans having been explained. This action on the fish showed that the hemoglobin carried cyanide instead of oxygen to the portions of the body where oxygen was needed.

The cyono-hemoglobin, which must have formed, can be reconverted to hemoglobin if the fish have not been subject to the cyanide for too long a period of time. They may be revived in fresh water, if there is any signs of life, in a short time.

Some important results that Professor Karsten found in his experiment with cyanide wastes and fish life are:

1. Acids, ferrous sulphate and potassium permanganate cannot be used to destroy cyanide to the point at which it no longer affects trout. An excess of acids or permanganate may be detrimental and cannot be used unless destroyed before reaching the stream.
2. Acids, ferrous sulphate and potassium permanganate can be used for reducing the stream-effluent ratio. If used for this purpose it may become possible for cyanide discharging industries to use streams that might otherwise be too small to dilute the cyanide effluent to the point at which non-effectiveness to trout is realized.

3. Cyanide in a stream does not affect the oxygen content for the reason that the atmospheric oxygen maintains the solubility equilibrium by furnishing oxygen at a rate greater than that of removal due to the formation of cyanate.

DISCUSSION OF THE METHODS OF WASTE DISPOSAL

PONDING

One of the original methods of cyanide waste disposal is ponding. This method is also used today, as a good treatment of cyanide has yet to be found. Ponding is a simple method to use. Earthen dikes are built around an area of land. These areas are inclosed by a strong fance and must have signs posted on them stating the character of the waste in the area. Each of these areas should be divided into several ponds so that the wastes will not have to be emptyed into a pond until that pond has stood long enough for tests to reveal that all the cyanide has been removed from it. The volume and number of ponds depends upon the volume of waste produced. The cyanide content of the waste material in these ponds will gradually decrease and finally disappear entirely if no fresh waste is added to the pond.

The removal of the cyanide is due to several factors. They are mainly: dilution by rain water, seepage, and destruction of the cyanide by either oxidation, hydrolysis, or decomposition.

The time required for the complete removal of the cyanide from the ponds is not definitely known as it undoubtedly depends upon a number of factors. These being rainfall, temperature, and type of soil, and other factors caused by local conditions.

The method of ponding should be considered as the next step better than the discharge of the wastes directly into streams, as it has mony objections. Concrete will stop the objection of seepage, but seepage is one of the factors for the removal of cyanide and yet is one of its objections. If seepage is allowed it might contaminate wells in the vicinity, or it might gain access to swimming holes or any number of things that humans might come in contact with. There are also other objections which aid in the removal of the cyanide and yet are an objection because of the danger that they cause.

DILUTION

Dilution is probably the easiest method of handling the cyanide wastes from the industrial plants. This is done by discharging the wastes into rivers, lakes, or sewers. However plating room wastes run on average about 400 to 500 p.p.m. of cyanide and the approximate toxicity threshold for cyanide is one or less p.p.m.. Therefore it would be very hard for a plant to dilute their wastes enough so only to contain one or less p.p.m. of cyanide.

The discharging of cyanide wastes into a stream is very dangerous unless the volume of the stream is at all times sufficient to reduce the cyanide below the fatal dose for aquatic life. Also the waste would have to be dispersed so as the local concentration of the cyanide would be prevented. The running of the cyanide wastes into the sewer makes another problem for the sewage plant to solve. Cyanide inhibits the digestion of sewage sludge. If cyanide wastes were continually discharged as would be the case in actual prectice, the inhibiting effect would be continuous and sludge digestion would be considerably impeded if not entirely checked.

There is not a point in favor of the disposal of cyanide wastes by the method of dilution. There are too many things against the use of this method and it should never be used by any plant for the disposal of cyanide wastes, except when the body of water, that the waste is emptyed into, is so great that no harm is done.

ACID TREATMENT AND AERATION

The removal of cyanide from wastes may be accomplished by means of a commercial sulphuric acid treatment followed by the volalitization of the hydrocyanic acid gas that is formed. During the process compressed air should be introduced through pipes in the bottom of the tank.

The success of this treatment depends upon, mainly, four main factors; 1. the acid concentration, 2. the period of aeration (a total of 16 hours is usually sufficient) 3. The completeness of cyanide removal, and 4. the toxicity of the remaining waste.

Usually the volume of the cyanide waste is comparatively small but uou should segregate all wastes not containing cyanides from the cyanide bearing wastes. One other important factor in designing the size of treatment plant needed is the volume of wastes to be treated. A weir box in the sewer line at some convenient point will be needed to determine the flow of wastes. Spoiled wastes volume may be determined by computing the volume of the vats that contain the wastes.

The hydrocyanic gas produced by this treatment process is very poisonous and therefore the location and design of the equipment must be such that the danger from these fumes is a minimum.

The treatment plant should consist of a rubber lined tank of sufficient capacity to hold the daily volume of waste. The cover of the tank should fit tightly. This cover should have a dome in the center which is connected to a tall stack.

The wastes may either be pumped into the tank from a sump connected to the factory drain, or they may flow in by gravity. The commercial sulpheric acid should be introduced into the tank, from a carboy, by means of a perforated lead pipe located in the tank above the surface of the waste solutions. The only danger in handling the acid is the adding of it too fast. This would cause too great an evolution of gas and might cause trouble by not being sufficiently diluted with ari.

Compressed air is to be introduced through perforated lead pipes laid in the floor of the tank. Diffusion plates may be used instead of lead pipes if so desired. In order to further dilute the gas, a blower should be located so as to blow a large volume of air into the side of the stack. The height of the stack should be at least forty feet high in order to get the gases up above most surrounding buildings. If there are any existing boiler stacks near they might be used.

The treated wastes may be emptied into a stream after a test shows the desired reduction in the cyanide content.

OXIDATION WITH POTASSIUM PERMANGANATE

Potassium permanganate will oxidize the cyanides in neutral or alkaline solutions with the production of cyanates.

$$3KCN \quad 2KMnO_4 \quad 3H_2O \quad 2Mn(OH)_4 \quad 2KOH \quad 5KOCN$$

Using the molecular weights of the above you find that according to this equation, 1.62 parts by weight of $KMnO_4$ is required to exactly oxidize one part of KCN or its equivalent of some other cyanide.

Tests have shown that the use of potassium permanganate is entirely practical from the standpoint of operation and cost of operation.

However, the wastes are somewhat toxic after the treatment if they are emptied undiluted into a stream, lake, etc.. This is found to be especially true if the wastes are not aerated.

Dr. Hubbs of the University of Michigan found that if the wastes were diluted one to one they would not kill fish as had the wastes before they were diluted. In a large stream this dilution would probably not have to be made.

In designing a plant for cyanide wastes treatment by the permanganate method you should build a tank having a hopper bottom for the collection of the sludge. this tank does not have to be covered as in the acid treatmânt method as there are no dangerous gases to contend with. The mixing of the permanganate and wastes in the tank can be accomplished by means of diffused air as in the acid treatment plant. There should also be a sludge bed of underdrained sand provided for the dewatering of the sludge.

The tank may be filled during the day and then treated just before closing time at night. The aeration may continue for a short time so that the wastes and permanganate are throughly mixed. The sludge may be drawn off the next morning.

The cost of the acid treatment and permanganate treatment plants will run about the same. The cost of construction of the acid treatment plant being more than the cost of construction of the permanganate treatment plant. However, the cost of operation of the permanganate plant will run somewhat higher than the cost of operation of the acid treatment plant.

TREATMENT WITH FERROUS SULPHATE

Ferrous sulphate was tried as a means of reducing the cyanide to some harmless form. This method was tried because it was thought that this method might be quick and also cost less than any other method used at this time.

Some of the facts found out about this method are that: when an excess of alkali is used, the amount of ferrocyanide formed is less than when smaller amounts of alkali are present; that a rise of temperature above 20°C is harmful to the reaction; that the results are independant of the dilution; that the reactions ase as complete in 5 to 10 seconds as they are after long standing; that unless the alkalinity is most carefully adjusted to suit the amount of iron used, an excess of ferrous solution gives no better results than the theoretical quantity, that is required by the equation:

$$\mathrm{6KCN} \qquad \mathrm{2FeSO_4 \cdot 7H_2O} \qquad \mathrm{K_2Fe(FeCN_6)} \qquad \mathrm{2K_2SO_4}$$

According to Professor Karsten as far as his experiment went, he did not find the ferrous sulphate treatment as good as thought, because it did not remove the cyanide to a great enough degree. The remaining cyanide was found to be around 4 p.p.m. and this is enough cyanide to kill fish in about fifteen to twenty minutes.

METHODS OF DETERMINING CYANIDE

An important factor in work of this kind is the determining the manner in which the results are to be checked after the treatment has been made. Most tests that are used with cyanide will give the same reaction with other radicals. There are six tests that give fairly good results, the Schonbein test using guaiac paper, the phenophthalin test, the prussian bule method, the silver cyanide method, the silver nitrate test, and the thiocyanate test which is specific for cyanides and is more sensitive than all the others. These tests are made as follows:

(1) The guaiac paper in the Schonbein test is prepared b saturation of strips of filter paper with 10 percent alcbholic tincture of resin of guaiac which is freshly prepared. These strips are dried and placed in a stoppered vial. They are moisteded with a one to 1000 solution of $CuSO_4$ when they are used.

The sample to be tested is placed in a flask and acidified with tartaric acid. The flask is closed with a corkiin the bottom of which is a slit for holding the moistened paper above the solution. The contents are warmed over a water bath and a blue or blue-green color of the paper indicated that cyanide is present.

(2) The phenophthalin test is sensitive if the proper precautions are ta en. If is a good method for determining small quantities of the cyanide. This test depends upon the production of a red color by the

oxidation of an alkaline solution of phenophthalin to phenolphthalein in the presence of a cyanide and a weak solution of a cupric salt. This test is not specificly for cyanides, as other compounds are able to oxidize the phenolphthalin under these conditions and give a positive reaction.

(3) The Prussian Blue method is specific for cyanides and depends upon the formation of a ferrocyanide. This takes place when an alkaline solution of an easily decomposable cyanide is warmed with a solution of ferrous sulphate. For low concentrations of cyanide this method is very good but for large amounts of cyanide the Prussian Blue method gives a very dense blue precipitate.

(4) The Silver Cyanide method depends upon the opalescence produced when and excess of silver nitrate is added to a slightly acid solution of cyanide. This test is not specificly for cyanides, as halogen acids and their salts or certain fatty acids will also produce opalescence with silver nitrate.

(5) This test is the same as is used for chlorides in water analysis. This is the Silver Nitrate test which is also used by many to determine the presence of cyanide. However the chlorides interfere with this determination and it cannot be used if hydrochloric acid or its salts have access to the waste. The end point of the silver nitrate determination is not as well defined in this case as is obtained about halfway through the titration or

just after the double salt formation is complete.

(6) The Thiocyanate test which is also specific for cyanides was found to be 5 to 10 times as sensitive as the Prussian Blue test. The Thiocyanate test depends upon matching of the color of the unknown sample and the colors of the standards. This colormetric method is also used with the Prussian Blue test, the silver cyanide test and the Phenophthalin test. It has been found that the Thiocyanate test will detect .000005 grams of CN in 10 ml. and less than this amount if the volume of the unknown sample is reduced to one or two cubic centimeters. This is the test used in this experiment and the results found were very satisfactory.

THE EXPERIMENTAL WORK

There were three main things wanted in the work on cyanide wastes. 1. If lime-sulphur could be used to treat cyanide wastes of high concentrations and reduce their toxicity far enough to make them safe to be emptyed into streams, lakes, or ponds. 2. If time was a factor. That is if the length of time in the treatment of the wastes by lime-sulphur had any effect on the results. Whether the wastes had to stand for one hour or 24 hours after the lime-sulphur had been added to them. And 3. if small concentrations of cyanide wastes could be treated. These wastes that contained around 500 p.p.m. of cyanide. Cyanide wastes of this concentration being found more often than wastes of higher concentration.

So as to be able to determine the value of a lime-sulphur solution in treating cyanide wastes, a known concentration of cyanide was made up. This was treated with the lime-sulphur solution, and then the amount of KCNS present was determined by analysis.

The lime-sulphur solution that was used was purchased from the Carrier-Stephens Chemical Company, Lansing, Michigan. The chemical analysis of it is as follows:

Calcium Polysulphide	30.0%
Calcium Thiesulphate	1.5%
Water and other inert ingredients	68.5%
Lime and Sulphur in solution	31.5%
Sulphur	24.0%
Baume 32 degrees at 15°C	

In order that a person might have an idea of what range of standards that were necessary for the determination of the cyanide that remained, a rough treatment was first made. The solution of KCNS was made up so that 1 ml. of KCNS was equal to 1 mg. of KCN. By using their molecular weights it was found that 1.4924 gms. of KCNS in 1 liter of solution should be used. The solution of KCN, that was used, was a 10% solution. This consisted of weighing out 100 gms. of KCN and making up the solution to 1 liter.

This first set of determinations consisted of taking 50 ml. portions of a 10% solution of KCN and adding varying amounts of lime-sulphur solution, letting these samples stand for 24 hours and then running a rough determination by use of the thiocyanate method. The standards deoded upon had a range of .5 ml. to 5 ml. of KCNS. In that range there were ten different standards with each standard increasing in the amount of KCNS by .5 ml.. The preparation of the standards will be discussed in detail later.

This rough determination showed that the range, of the standards to be used in further experiment, was between 1 ml. and 2 ml. of KCNS used in each standard.

The first accurate determination was made as follows: An accurate prepared 10% KCN solution was distributed in 50 ml. portions into 5 beakers. A sixth beaker containing 50 ml. of distilled water was used as a blank treatment to see if it contained any cyanide. To all of these beakers, lime-sulphur was added in varying amounts as follows.

Beaker No.	Ml. of KCN solution	Ml. of lime-sulphur
1	50 water blank	6
2	50	6
3	50	7
4	50	8
5	50	9
6	50	10

When the lime-sulphur solution was added there were two things noted. One was that there was a precipitate formed and that each solution changed to a yellow color. However this color gradually disapeared in the beakers containing 6, 7, 8, ml. of lime-sulphur. Beakers No. 6 which had 10 ml. of lime-sulphur in it remained a yellow color. This leads one to believe that there was an excess of lime-sulphur added so that upon carrying out the tests for cyanide there should be a 100% reduction of cyanide in that beaker. The amount of precipitate increases also as the amount of lime-sulphur added increases. Second that all of the samples gave off H_2S gas upon the addition of the lime-sulphur solution.

These samples were covered with watch glasses and were left to stand for 24 hours. At the end of this period of time the samples were filtered to remove the precipitate. Then the solutions were diluted to prepare for the determination of the remaining cyanide. The dilutions used in the rough treatment were used again here as the range of the standards had been determined from the rough treatment trial. 5 ml. of this solution was pipetted into a 200 ml. flask and made up to the 200 ml. mark. Then after being throughly mixed, 10 ml.

of this was taken and diluted to 100 ml.. This last dilution was mainly a convenience as the amount of this solution used in the nessler tube was 10 ml. and this made a resulting dilution of 40 to 1.

After the second dilution was made, HCl was added so that the solution was just acid to litmus. This was done to remove any excess sulphur which might be present and which would interfere with the analysis. The acidified sample was heated gently to coagulate the sulphur and also to remove any H_2S gas that might still be present, (J. W. Foshen and co-authors, Childs and Ball found that heat did not drive off any appreciable amounts of cyanide). I also assumed that bringing these solutions to a temperature that would drive off the H_2S gas would not drive off any cyanide. When the sulphur had been coagulated and there was not any further odor of H_2S the samples were allowed to cool. They were then filtered to remove the sulphur. The samples were now ready for the determination of the amount of KCNS present in them.

It was found out by experience that if the 1 ml. of ferric chloride solution was not added to the sample until the standards were made up that the results would be better. As soon as you add the ferric chloride to either the samples or the standards their color will begin to become fainter upon standing a few minutes. That is the reason, I believe, for the first two trials being low. If the samples or standards are allowed to stand over night, the color will be almost entirely gone by the next morning.

At this point in the determination the standards were made up so that the ferric chloride could be added to the samples and standards at approximately the same time.

The solutions that were used in the preparation of the standards are as follows:

1. A 5% hydrochloric acid solution
2. A 10% ferric chloride solution
3. A standard solution of KCNS prepared so that 1 ml. of the solution was equal to 1 mg. of KCN.

Nessler tubes were used to hold the amounts of standard solutions and also the samples. The range of standards used in the first four trials was from 1 ml. of KCNS to 2 ml. of KCNS and varied from each other by .2 ml..

The amounts of KCNS, to give the desired range, were placed in the tubes and diluted to about 60 ml. with distilled water. The solutions were then acidified with 1 ml. of the 5% HCl solution. The 1 ml. of 10% solution of ferric chloride was added to both the samples and the standards. Both were adjusted accouately to 100 ml., and all solutions were then inverted so as to mix them well.

The samples were compared to the standards by comparing the colors. The matching colors representing the amount of KCNS present.

The samples that had the largest amount of lime-sulphur added to them showed the deepest color when comparing with the standards. This proved that the more lime-sulphur added to the sample the more KCN that was converted to KCNS until 100% of the KCN had been converted to the KCNS.

The first trial made after the rough trial is shown on the top of the third page of the experimental work. Trial number two was also made using six samples. One of these again being a sample of distilled water. Trials three and four were made using nine samples. These nine samples ranged from three through eleven ml. of lime-sulphur used in them. Each differing from the preceeding one by one ml.

There were two things that had to be corrected for in figuring out the results, so as to have an accurate figure for the percent of the cyanide removed. One was the purity of the KCN used. The other was to find out how much moisture the KCN contained.

The KCN used had a purity of 95% and the moisture present in the KCN was so small that it did not effect the results. The obtained results, therefore, were divided by .95 to corredt for the purity and give the actual results.

The results of this first part of the experiment are listed below and are self explanatory.

Part 1

In part 1 all these results are based on the 24 hour samples.

Sample Number	1	2	3	4	5	6	7	8	9	10
Strength of sample	All samples were of 10% strength									
Ml. of sample used	50 ml. of sample in each									
Ml. of Lime-Sulphur	6	6	7	8	9	10				
	6	6	7	8	9	10				
	2	3	4	5	6	7	8	9	10	11
	2	3	4	5	6	7	8	9	10	11
Mg. of KCN in portion tested	0	2.23	2.19	2.15	2.12	2.08				
	0	2.23	2.19	2.15	2.12	2.08				
	2.40	2.36	2.32	2.27	2.23	2.19	2.15	2.12	2.08	2.05
	2.40	2.36	2.32	2.27	2.23	2.19	2.15	2.12	2.08	2.05
Mg. of Converted KCN	0	1.0	1.1	1.3	1.5	1.8				
	0	1.1	1.3	1.6	1.8	2.0				
	.5	.6	.8	1.0	1.2	1.4	1.6	1.8	2.0	2.1
	.4	.6	.8	1.0	1.3	1.4	1.6	1.8	2.0	2.0
% converted to CNS	0	44.8	50.2	60.4	70.8	86.6				
	0	49.3	59.3	74.5	85.0	96.2				
	20.8	25.4	34.5	44.2	53.9	63.8	74.4	85.0	96.2	102
	16.7	25.4	34.5	44.2	58.4	63.8	74.4	85.0	96.2	97.5
% converted to CNS corrected for 95% purity of KCN	0	47.2	52.8	63.6	74.6	91.2				
	0	52.0	62.4	78.4	89.4	101.1				
	21.9	26.8	36.3	46.4	56.7	67.3	78.4	89.4	101.1	108
	17.6	26.8	36.3	46.4	61.4	67.3	78.4	89.4	101.1	102.5

The second stage of the experiment was to determine if the length of time, after the addition of the lime-sulphur had any effect upon the results. It was proven that one hour of time was as good as 24 hours.

In each of the determinations in the first part, a portion of the sample was tested for $KCNS$ after 1 hour and another portion was tested for $KCNS$ 24 hours later. The results in each case were the same. The only error that was found in the experiment has been explained as error due to the making up of the standards or samples before being ready to compare. This time lapse being responsible for the change in color of the samples and standards and therefore making an error in the results.

Below is a chart of the results made after 1 hour and those made 24 hours later. Each is marked as to its respective time.

From the chart you may notice that the first trial did not have as good results as the last three trials. This is the one that had the error due to the fading of color of the standards. The samples in this case had the ferric chloride added to them before the standards were made up and therefore when compared with the standards they compared favorably with those giving low results.

The water blank that was carried along with each trial did not show any signs of cyanide. In each trial the blank was tested as the samples were and there was no positive water blanks found in any of the trials.

Part 2

Sample Number	1	2	3	4	5	6	7	8	9	10
Ml. of Lime-Sulphur	2	3	4	5	6	7	8	9	10	11
In 24 hrs. % converted to CNS and % corrected for purity of KCN				0	47.2	52.8	63.6	74.6	91.2	
				0	52.0	62.5	78.4	89.4	101.1	
	21.9	26.8	36.3	46.4	56.7	67.3	78.4	89.4	101.1	108
	17.6	26.8	36.3	46.4	61.4	67.4	78.4	89.4	101.1	102.5
In 1 hr. % converted to CNS and % corrected for purity of KCN				0	52.0	52.8	63.6	89.4	91.2	
				0	56.7	62.4	78.4	89.4	101.1	
	21.9	26.8	36.3	46.4	61.4	67.3	78.4	84.5	101.1	102.5
	21.9	26.8	40.8	46.4	61.4	67.3	78.4	89.4	101.1	102.5

The results as a whole check quite closely. The error that there is, is probably due to error caused by my-self in reading the standards. However the error in the first two samples has been explained as due to fading of the color of the samples.

Part three was to find out if small concentrations of cyanide wastes could be treated. Three different concentrations were used in this part of the experiment. One had a KCN concentration of 500 p.p.m., the second was 1000 p.p.m., and the third was a concentration of 2000 p.p.m. of cyanide. That was the same as making up concentrations of KCN of .05%, .1%, and .2% solutions. The procedure was much the same as the one on the higher concentrations, differing only with the amount of lime-sulphur added and the dilutiions made. With all three of the concentrations, 100 ml. samples were used.

The amount of lime-sulphur used in the .05% sample was .1, .2, and .3 ml.. With the .1% sample, the lime-sulphur used was .2, .3, and .4 ml. and .4, .5, and .6 ml. of lime-sulphur were used with the.2% solution.

The dilutions were made such that they would form concentrations that would fall in the range of standards that contained from .2 through .6 ml. of KCNS.

Upon the addition of the lime-sulphur, to these small concentrations, it was observed that there was no noticeable precipitate. However the time element did not effect these samples either, according to the results. It was also hard to detect any noticeable H_2S gas from the samples.

The only objectable thing in making the tests for KCNS where such small concentrations of KCN are used is that you are working all the time with tenths of a ml..

The difference in color can not be distinguished very easily unless the standards differ by .1 ml. of KCNS, but a difference of .1 ml. of KCNS makes quite a difference in the results of the percentage of cyanide removed when working with concentrations of 500 p.p.m.. However the results of the work on small concentrations are satisfactory.

In working with the .05% solution of KCN, to which was added .1, .2, and .3 ml. of lime-sulphur, it was found that the 100 ml sample to which .1 ml. of lime-sulphur was added that the yellow color left it after about one hour. This showed that there was probably not 100% reduction of the KCN. This was proven by the results. The yellow color of the sample that contained .3 ml. of lime-sulphur remained and in this case there was an excess of lime-sulphur.

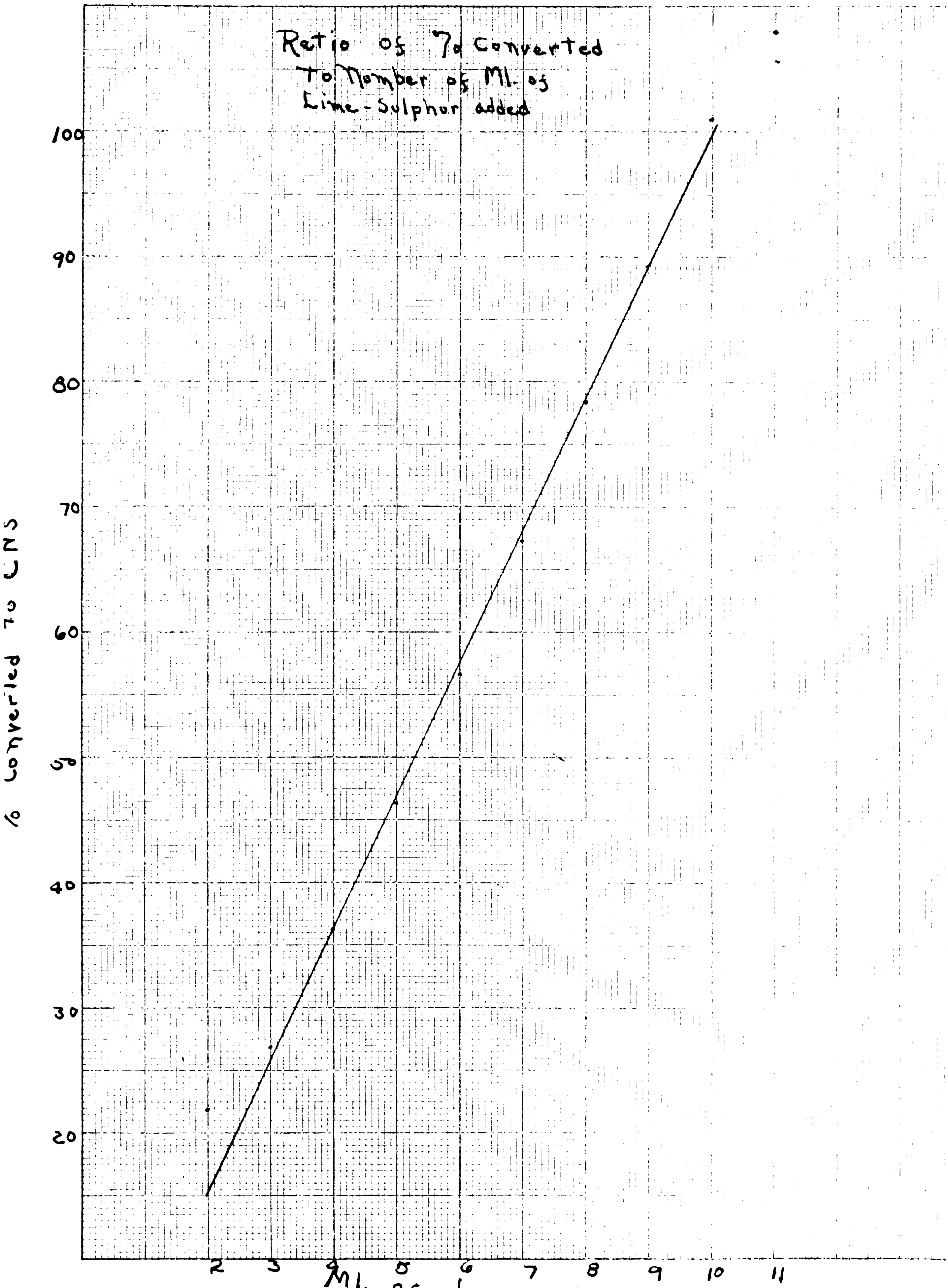
In the case of .1% and .2% solutions, simular results were found. The sample containing the smaller amount of lime-sulphur lost its color in about one hour and the samples containing the larger amount of lime-sulphur retained their color.

The results of part three of this determinations are listed below and are self explainatory.

Part 3

100 ml. samples used in each case dilutions made so as the same standards could be used in each case.

	1 hour samples			24 hour samples		
Strength of sample used	.05%			.05%		
	.10%			.10%		
	.20%			.20%		
Ml. of Lime-Sulphur	.1	.2	.3	.1	.2	.3
	.2	.3	.4	.2	.3	.4
	.4	.5	.6	.4	.5	.6
Mg. of KCN in portion tested	.499	.499	.498	.499	.499	.498
	.499	.498	.498	.499	.498	.498
	.498	.498	.497	.498	.498	.497
Mg. of converted KCN	.3	.4	.5	.4	.4	.5
	.4	.4	.5	.3	.5	.5
	.4	.4	.5	.3	.4	.5
	.3	.4	.5	.4	.45	.5
	.4	.45	.5	.3	.4	.5
	.4	.4	.5	.4	.4	.4
% converted to CNS	60.1	80.3	100.2	80.3	80.3	100.2
	80.3	80.3	100.2	60.1	100.1	100.2
	80.2	80.3	100.2	60.2	80.3	100.2
	60.2	80.3	100.2	80.2	90.3	100.3
	80.3	90.3	100.5	60.4	80.3	100.5
	80.3	80.3	100.5	80.3	80.3	100.5
% converted to CNS corrected for 95% purity of KCN	63.3	84.4	105.3	84.4	84.4	105.3
	84.4	84.4	105.3	63.3	105.4	105.3
	84.4	84.5	105.6	63.3	84.5	105.6
	63.3	84.5	105.6	84.4	95.2	105.6
	84.5	95.2	105.9	64.6	84.5	105.9
	84.5	84.5	105.9	84.5	84.5	105.9



Ratio of % Converted To Number of Ml. of Lime-Sulphur added

INTERPRETATION OF RESULTS

The results obtained in the course of experiment were very successful in most cases. By turning to the graph on the preceeding page you are able to get a good picture of the results obtained by the use of varying amounts of lime-sulphur with the 10% KCN solution. The best idea on how much cyanide was actually removed from the solutions is obtained by referring to the column in the tables giving the percent of cyanide removed. The amount of cyanide removed increases as the amount of lime-sulphur solution added increases. This, of course, is only natural and what you would expect. The results with the 10% solution of KCN proved that lime-sulphur may be used to treat high concentrations of cyanide wastes.

The percent of cyanide removed after one hour was the same as the percent removed after 24 hours. This proved that, by the use of lime-sulphur in the treatment of cyanide wastes, a plant could treat its wastes in a very short period of time. This is very advantageous to a plant having a large volume of wastes. This also cuts down on the size of the treatment plant needed. So the cost of a waste treatment plant, if lime-sulphur is used, will be quite reasonable.

The third part of the experiment dealt with small concentrations of cyanide wastes. The smaller of the concentrations of KCN used was 500 p.p.m. and this is still somewhat larger than the average concentration of cyanide found in the average waste. At this small concentration every measurment was in tenths of a ml.. It is very hard to do accurate work using such small measurments. The results obtained were satisfactory as to the percent of cyanide removed. However if a part of a drop in excess was added it would throw the results off. One drop might contain one or more tenths of a ml.. Yet from the results obtained from the work on such small concentrations one would be led to believe that small concentrations of cyanide wastes could be treated with good results.

CONCLUSIONS

From the experimental results, it appears that the lime-sulphur does have the ability to convert the cyanide to a cyanate or thiocyanate which is stable and not toxic to humans, animals, or fish.

After the sludge has been removed from the treated solutions, the effluent may be diluted safely by letting it flow into a stream or lake. The reaction that takes place upon the addition of the lime-sulphur is not a violent one. The only problem to be encountered is the formation of the sludge. On low concentrations of cyanide the sludge will be very small in comparison to the volume of wastes and it seems that it could be dumped into the river along with the treated liquid. However, if possible it might be drawn off and placed on a drying bed to remove the moisture. The residue then could be disposed of in a manner desired by the plant. If the concentration of the cyanide runs up around 20,000p.p.m. the volume of sludge will be greater and if emptyed into a stream it might cause a scum and deposits along the banks. This is to be avoided if possible.

In a paper published by the Olds Motor Works of Lansing, Michigan, they stated that the sludge they had after using the lime-sulphur was composed of:

1. Calcium Thiocyanate
2. Sodium Thiocyanate
3. Calcium Cyanamide
4. Sodium Carbonate
5. Sodium Sulphide

The main trouble, with the use of lime-sulphur in the treatment of cyanide wastes, is that if there are other wastes present the results will no be as desired. The Ford Motor Company, Dearborn, Michigan tried to use lime-sulphur. Their results were unsatisfactory because of other wastes present. For example, they had a chromate waste present. When the wastes were treated the precipitate was so dense that the problem of its disposal was as great as the original problem itself.

The lime-sulphur treatment should not be used if the wastes are a combination of several types. Another method might be better. The acid treatment with all its faults does definitely lower the concentration of cyanide and if it were not for the personal hazards it would probably be the best method.

If there had been more time to make further experimentation with this method, it might have been well to carry out the treatment of a combination of wastes. Wastes which would be simular to wastes encountered in most plants. The one thing sure from the work on the treatment of cyanide wastes with lime-sulphur is that high concentrations can be treated very well and with good results. The limit or the lowest concentration of cyanide that can be treated with good results is still some in doubt as you are working with such small measurments that one is not sure that his results are correct. The time limit or time factor has been shown not to be important if it is over one hour. Therefore the writer believes that the things desired have been proven but that there are several other questions that will have to be proven before lime-sulphur may be used by all plants in treating their cyanide wastes.

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