NEUTRALIZATION AND UTILIZATION OF PICKLING LIQUORS

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Neutralization and Utilization of Pickling Liquors

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INTRODUCTION

At the present time there is considerable discussion and debate concerning stream pollution by those groups of persons so interested. It is especially prevalent in our State of Michigan because of its position as a resort state and also because it is a state which is well industrialized.

Currently, there is quite an issue between persons connected with various conservation leagues, resort organizations, and allied sportsmen's groups and the industrialists. The former wish to maintain and preserve wildlife and stop further stream pollution. The industrialists agree with this idea, as many of them, no doubt, are keen sportsmen. However, as is the case in many problems, money is the big talking point, since in many cases, it would entail the outlay of large sums of money to treat the wastes for suitable disposal.

It is not the intention of the writer to use this paper as an argument in support of either side of the issue, but merely to present an investigation of this particular phase of the tremendous problem of waste disposal and stream pollution.

This is not a problem which is faced by this state alone. It is a problem which is challanging the whole world. Neither is it a new problem. Scientifically minded men have been seeking a solution to the problem of the disposal of waste pickle liquor for more than fifty years in an effort to perfect processes which will operate satisfactorily not only from a technical standpoint but also an economic one.

Treatment of acid wastes from iron industries seemed to have started first in England around the year, 1888. However, in the United States, investigations of the problem were in progress as early as 1890. However, the use of steel and iron products has increased tremendously since the turn of the century, thereby increasing the size of the problem. The use and manufacture of these products has spread considerably also, treatment being necessary in connection with the Ruhr river in Germany and places as distant as Bombay, India.

The waste liquor may be disposed of by several methods without treatment, such as pumping it into deep wells, abandoned mines or evaporation ponds. Generally, all methods such as these give rise to situations which are objectionable. Probably the method which is most objectionable is the one whereby the waste is transmitted directly to a body of water such as a stream or lake. This last method gives rise to the viewpoint from which the rest of this paper is written.

TYPES of PICKLING LIQUORS and COMPOSITION

Waste pickling liquors are composed of acid and alkali solutions. Metal has to be cleaned before it is used in manufacturing parts. It may be cleaned by the use of sulphuric acid either by still pickling or electrolytic pickling. Red rust is removed from iron by still pickling. In this process, the iron is immersed in a 4 to 5 per cent solution of sulphuric acid, which is heated to a temperature of 160 to 170 degrees F. The metal is taken out after abour 1½ hours, which is the time required for cleaning, and put in a vat which has a continual source of clean water. It is then put into a solution containing ½ per cent caustic soda and 3/4 per cent trisodium sulphate. The electrolytic method is usually used to clean off the black magnetic oxide, since the still pickling method is too slow. The electrolytic method is about the same as the still method with the exception that the metal is an anode and the acid solution is stronger. It is these above processes which produce the waste which must be disposed of.

Either process produces acid and alkali solutions and also soluble ferrous sulphate. The acid solution is usually thrown away after it is lowered to an acid content of approximately 2 per cent. The wash waters also contain acid. More sulphuric acid is produced when, as the acid is neutralized, the ferrous sulphate is precipitated which is hydrolized to form ferrous hydroxide and sulphuric acid. The alkali solutions are used to clean the grease from the metal parts and to neutralize the acid on them.

NEED for TREATMENT

Treatment of the waste is needed for the reuse of the material and in other cases for the by-products obtained. There are cases where the by-products obtained, are valuable enough to pay for the cost of treatment. There are a great number of processes which have been developed for the recovery of useful products. However, the forty-odd processes, only a few of these have been successfully operated and some of these are limited by fifferent factors, as for instance in the case of recovery of copperas from pickle liquor. This process is not a difficult one. The limiting factor is an economic one, in that the total demand is met by a supply which utilizes somewhere in the neighborhood of 4 per cent of the total of waste pickling liquor. However, even in cases where reuse and recovery products do not in themselves make treatment economically gainfull, treatment should be carried on for the prevention of stream pollution.

Pollution from these wastes has many effects. There is, of course, a public health menace. Probably no one would drink any of the polluted water supply direct. There might be the possibility of its effect on livestock from drinking. Swimmers might come in contact with the sulphuric acid and in such case suffer from its damaging action on animal tissue. Pollution of this type is unfavorable from an esthetic standpoint in that the ferrous hydroxide oxydizes to form ferric oxide which is insoluble. The ferric hydroxide being insoluble settles out on the bottom of the stream. This brings about a condition which is not only very unsightly but is also an extremely unfavorable condition for the propagation of fish and other aquatic life. From a recreational standpoint this polluting agent creates a situation which is not advantageous to boating enthusiasts. The sulphuric acid has the ability to react with the paint on the boats with undesired results. From a more utilitarian standpoint, there is the effect of pickling liquor in water supply.

For coagulation and sedimentation in the clarifying treatment of turbid waters when alum is used, there may be an added cost to raise the pH value of the water. Since, when alum is used for clarification, the reaction takes place when the pH of the water is alkaline. In most cases, this would probably require the use of larger amounts of soda ash (sodium carbonate) for the reaction and clarification to take place than would be necessary if the raw water supply were in a condition uncontaminated by the disposal into it of the waste pickling liquor. Still another detriment added to the raw water supply by this pollution is an increase in corrosiveness, especially in boilers.

Since corrosive action on metals by water takes place when the water contains dissolved oxygen, and nearly all water does. This action takes place at a rate which is proportional to the temperature, hydrogen-ion concentration, and presence or lack of certain mineral salts. From this, the conclusion is drawn that the higher hydrogen-ion concentration (the lower the pH) the more corrosion that will take place in boilers and probably will necessitate additional water treatment to prevent boiler damage.

In cases where not all the iron is precipitated out before reaching the raw water intake, it may be necessary to treat the raw water for removal of the iron compound. Iron compounds in the water supply are objectionable for several reasons. They impart a hardness to the water which may be removed by the lime and soda ash process. If the iron compounds are not removed, they have the objectionable ability to stain everything with which they come in contact, especially washbowls, lavatories, and bathtubs. When the water is used for laundering, they are especially objectionable. The iron in the water may precipitate out of solution and settle in the mains where there is low velocity of flow. A sudden, higher demand for water may disturb these rust deposits enough so that the water supply users experience difficulty using the water. Iron - bearing water may interfere with cooking by turning vegetables dark when they are boiled. Iron compounds in the water supply may stimulate the growth of crenothrix or other bacteria which may cause the water to have objectionable tastes and odors. Crenothrix growths may become large enough to hinder the flow of water in the mains.

In cases where pickle liquor is treated in with domestic sewage, there are certain difficulties which may be encountered. If there is sufficient quantity of the pickle liquor to cause the entire flow of sewage to be acid, the biological processes of secondary treatment may be seriously interfered with. Where the activated sludge process is used, iron in the pickle liquor will seriously hamper the functioning of the aeration units by clogging the air diffusion equipment. It is an expensive procedure to clean or replace the air diffusers, which makes it important that an excessive amount of the pickle liquor does not get into the sewage treatment plant. In connection with the treatment of pickle liquor with domestic sewage, it should be noted that this waste has a disintegrating effect on pipes and equipment made of steel, cast iron or concrete due to the action on these materials by the sulphuric acid. Of the foregoing detriments which may be caused by waste pickle liquor probably none has an effect which is better known than that of stream pollution and its resultant consequences to wildlife.

Of all the dangers of pollution, probably none has been commented on or has been the subject of as many articles written for the layman as the danger to wildlife and in this case most always the wildlife referred to is the fish population. The fish population of any body of water is dependent upon not only the water there contained but is sustained and closely related to and a part of the myriad of organisms, plant and animal, whose habitat is that body of water. Since our streams and other bodies of water have a value from the fish life standpoint, not only as a source of recreation for sport fishing but also as source of food production through commercial fishing, these water bodies should not be mistreated. Whether or not a stream is to be polluted past the danger point for the aquatic organisms it contains must be determined by a balancing of values. The value of the body of water not only as a supporter of aquatic life but also, as previously discussed, a source of water supply and so forth must be weighed against the savings gained by non - treatment of the waste. These savings would mean a loss in value of a stream because it would mean a changing of the environment for the aquatic community which would kill off many of the organisms which can endure only limited deviations from an average set of complex environmental conditions.

Industrial wastes or municipal sewage may pollute a stream by several different means either singly or in combination. The latter condition is the greater evil. M. M. Ellis, Senior Aquatic Phipiologist of the U. S. Fish and Wildlife Service at the University of Missouri has classified pollution which would be hazardous to fishlife as follows:

(1) Settleable suspensoids which cover the stream bottom.

(2) Materials which undergo chemical changes requiring oxygen.

(3) Substances which change the pH of the water.

(4) Substances which change the salinity of the water.

(5) Materials which are of themselves toxic.

A combination of several of these conditions, none of which singly would be lethal, might cause death to fish life. Waste pickling liquor generally pollutes a stream by every one of the above mentioned methods, excepting the fourth.

When the ferrous hydroxide is oxidized, ferric oxide is formed. The ferric oxide is insoluble and settles out on the stream bottom. This will cause a situation which will make it impossible for the bottom fauna to be supported. Once the bottom fauna is smothered out, the food supply of the fish is gone.

The process by which the ferric oxide is formed from the ferrous hydroxide is also a bad situation from the oxygen demand standpoint.

This waste has a very high initial oxygen demand caused by the oxidation of the ferrous hydroxide to the ferric oxide. The danger in this situation would be to allow the dissolved oxygen in the water to go below 5 parts per million. If the dissolved oxygen level falls below 5 parts per million, even for only a few minutes, some of the fish start dying. The dissolved oxygen level preferrably should be maintained above this level. Many fish will live in water containing less than five parts per million of dissolved oxygen but certain of their physiological and biochemical processes are stopped or retarded. Also the fish's resistance to other hazards is reduced. One of such hazards may be a change in the pH of the water to one which would not be propitious for suitable environment.

When the pH of the water goes below 5.0, a condition exists which is dangerous and may kill the fish. This condition affects a fish by producing congested areas and stasis in the terminal portions of the gill filaments. This is a bad situation since the gills are a respiratory and excretory organ and as such, it is vital that the functioning of this organ be unimpaired. With the pH of the water below 5.0, the ability of the gills to absorb oxygen is impaired, some of the excretory cells stop functioning, and the flow of blood through the gills is retarded. Extremely small amounts of acid can, in some cases, cause an adverse pH condition.

The sulphuric acid may cause harm in addition to that caused by increasing the hydrogen-ion concentration of the water. It can be of its ownself toxic, if it occurs in a strong enough concentration. This would probably be a rare occurence, happening only if the diluting medium were small in volume or extremely slow moving.

The discussion has to this point, in the opinion of the writer, shown the need for treatment of spent pickle liquor in many cases. Some of the various processes and allied equipment used in the utilization and neutralization of waste pickling liquor will be the main theme for the rest of this Paper.

UTILIZATION PROCESSES

The first treatment process to be discussed is the one from which copperas is recovered. The spent pickling liquor is heated with scrap iron to neutralize the acid. The solution which results is allowed to stand, so that the suspended material may settle out. Then the copperas is crystalized by one of two methods, evaporation or refrigeration. It is possible, if the crystals are dried with care, to produce lower hydrates. However, the drying is not usually carried past the trihydrate. The copperas may be used in several ways. In the treatment of water and sewage, it may be used as a coagulating agent with lime or it may be used as in chlorinated copperas form. The above process is one of first developed for the treatment of waste pickling liquor. No free acid is recovered by this process.

Another process which is used is one in which both copperas and free sulphuric acid are produced. There are several variations of this type of process. However, they all have one thing in common and that is that part of the ferrous sulphate is removed as copperas and in some cases, sulphuric acid is added to the resulting liquor. This is then returned to the pickling vats for reuse. Most of them use cooling and some evaporation for crystallizing the ferrous sulphate.

There are marked differences in the types of processes as to equipment and operation used to separate a part of the ferrous sulphate from the waste pickling liquor. In some of the processes, sulphuric acid is mixed with waste pickling liquor. The resulting solution is then cooled. This gives a common ion effect which, when the liquor is cooled, increases the amound of copperas crystallized. In another process, the liquor is cooled to atmospheric temperature which crystallizes out a part of the copperas. Then the liquor is drawn off and concentrated sulphuric acid is added. Next this solution subjected to refrigeration which lowers the temperature to around 32 degrees F. and more copperas is obtained. After the liquor is withdrawn from the second yield of copperas, it is diluted with water to give the proper acid concentration and put back into the pickling vats.

In several of the processes, a part of the copperas, which has been recovered, is dried and mixed with the spent pickling liquor during one of the first stages of the process. The liquor is cooled in one to three stages.

A process which uses both crystallization and evaporation is the Butler - Little process. First the spent pickling liquor is sprayed into the top of a high round tower which has been lined with lead. A current of cool air is circulated up through this tower which vaporizes some of the moisture and cools the falling spray so that considerable quantities of copperas crystallize. The copperas is collected at the base of the tower in a cone - bottom tank. The suspension of copperas and pickle liquor is taken from this tank and the copperas removed by the use of a centrifuge. The liquor is then pumped back to the pickling vats.

Another process which is used is one involving evaporation.

The waste pickling liquor is clarified and placed in evaporation. The waste pickling liquor is clarified and placed in evaporators which are lined with lead. The pickle liquor is evaporated under vacuum so that the sulphuric acid reaches a concentration of about 28 per cent. The resulting liquor is drawn off and cooled. The copperas may then be separated centrifugally or by using a rotary filter. The liquor is then recirculated to the pickling vats.

Still another process developed in France uses a multijet vacuum evaporator and crystallizer which evaporates some of the water from the liquor in addition to cooling it. Some of the ferrous sulphate is crystallized. The ferrous sulphate is separated centrifugally from the liquor which is returned to the pickling vats.

The last process, to be discussed, for recovery of copperas and sulphuric acid is one which is quite different than the previous ones. This one is a patented one and was patented in Great Britain by de Lattre. A fatty alcohol is added to the liquor. Most of the ferrous sulphate precipitates as copperas, which is centrifugally separated from the liquor. Fractional distillation is used to reclaim the alcohol and free acid. The acid may then be returned to the pickling vats. The processes so far discussed have dealt with the treatment of waste pickling liquor so as to obtain copperas and sulphuric acid. Another way of treating the liquor is one in which ferric sulphate and sulphuric acid are obtained.

One method for obtaining the ferric sulphate is treating ferrous sulphate with oxygen and sulphur dioxide. Jets of air and sulphur dioxide come in contact with a ferrous sulphate solution resulting either from dissolving copperas in water or from waste pickling liquor. Ferric sulphate can be used for the treatment of sewage and purification of water with good results. It may be used alone or chlorinated and may reduce operating costs. Another treatment process of waste pickle liquor is one involving the recovery of sulphuric acid and iron oxide.

One method in treating the liquor for sulphuric acid and iron oxide is one in which the liquor is first neutralized with iron oxide. The resulting solution is evaporated directly and dried to ferrous sulphate monohydrate. The monohydrate is then mixed with a proper amount of iron disulphide and roasted. This roasting operation produces sulphur dioxide and iron oxide. Part of the iron oxide is used to neutralize the waste pickle liquor and the rest is marketed. It may be utilized as a paint pigment. The sulphur dioxide goes out with the furnace gases. The furnace gases are purified and the sulphur dioxide is made into sulphuric acid.

Another process which is used to revover iron oxide was developed in Germany. A proper amount of low - volatile, noncaking coal, which has been finely ground, is mixed with copperas. The copperas is obtained by one of the previously discussed process. The copperas is first dried to approximately the trihydrate, or it is possible to use a properly proportioned mixture of the monohydrate and heptahydrate. The mixture of the ferrous sulphate and coal is then roasted to final temperature of 1250 - 1300 degrees C. The iron sulphate breaks down into iron oxide, sulphur dioxide, and water vapor. The furnace gases are purified and used to make sulphuric acid. The iron oxide which remains in the furnace is sintered until a cinder is produced. This cinder is produced. This cinder is charged into a blast furnace.

A utilization process for the treatment of waste pickling liquor involving iron oxide is one resulting in an end product of iron oxide which is specifically used for a pigment. In this process, the free acid is neutralized with scrap iron and the solution clarified. This clarified solution is circulated to an atomizer and spray - dried. This operation produces ferrous sulphate monohydrate. The monohydrate is produced in the shape of minute spheres which are hollow. The ferrous sulphate is roasted and iron oxide paint pigments produced. The furnace gases can be used in the manufacture of sulphuric acid. A process similar to this may be used with accurate feed control and temperature control to produce a very fine iron oxide of uniform size which is free of grit. This product is valuable as glass - polishing rouge. By treating waste pickling liquor with calcium chloride and then calcining this product, iron oxide pigments of several different colors are manufactured. Several other processes have been developed involving treatment with sodium sulphate, zinc oxide, or soda ash.

One product derived from the treatment of waste pickling liquor uses the trade name "Ferron". It is used as a construction material. In the making of this material, the waste pickling liquor is first neutralized by adding mild of lime. This is done under carefully controlled conditions of pH, temperature, and concentration. A suspension results which consists of calcium sulfate and iron hydroxide. This suspension is filtered and the resulting cakes are put through a pug mill which extredes the material in the desired shape which is then dried at a temperature of about 175 degrees F. "Ferron" can sawed or machined and used as an interior construction material such as wallboard. The uses of materials manufactured from the treatment of the waste pickle liquor is quite wide, as for instance, the treatment process which produces ammonium sulphate.

Ammonium sulphate is manufactured in one process by flowing the pickling liquor down a vertical tower which has a stream of air and ammonia pumped up through the tower. A solution is formed which contains ammonium sulphate and iron oxide. The iron oxide is filtered out and can be sintered for use in a blast furnace. The ammonium sulphate is recovered from the filtrate.

The last utilization process for the treatment of waste pickling to be discussed, is one which is not too satisfactory and probably needs more experimentation. This process consists of treating the liquor with soda ash. From the resulting reaction, sodium sulphate and iron carbonate are recovered. The sodium sulphate is used in the manufacture of soda, glass, paper, dyes, soap, and other products. In spite of the use of this product by a wide variety of industries, the market is quite limited. The other product of this process, iron carbonate, is an expensive ore to process.

NEUTRALIZATION PROCESSES

Another branch of treatment processes consists of various means of neutralization. The first process to be discussed is the treatment of the waste pickling liquor with lime. The waste pickle liquor and rinse waters pickle liquor and rinse waters are pumped to a large tank where a lime slurry is added. This mixture is then pumped to another tank where it is thoroughly agitated. It is then transferred to another tank where clarification takes place as the sludge is precipitated. The sludge is mechanically collected and transferred to a drying lagoon. The clarified effluent can be discharged to a body of water without danger of pollution. The lime slurry acts with both the acid and iron compounds. about 1/5 of the slurry acts to neutralize the acid and the rest precipitates the iron. The main disadvantage of this process is that it is expensive. In some cases the cost of treatment can be as expensive as the cost of the pickling process. Another neutralization treatment which is used involves the use of limestone.

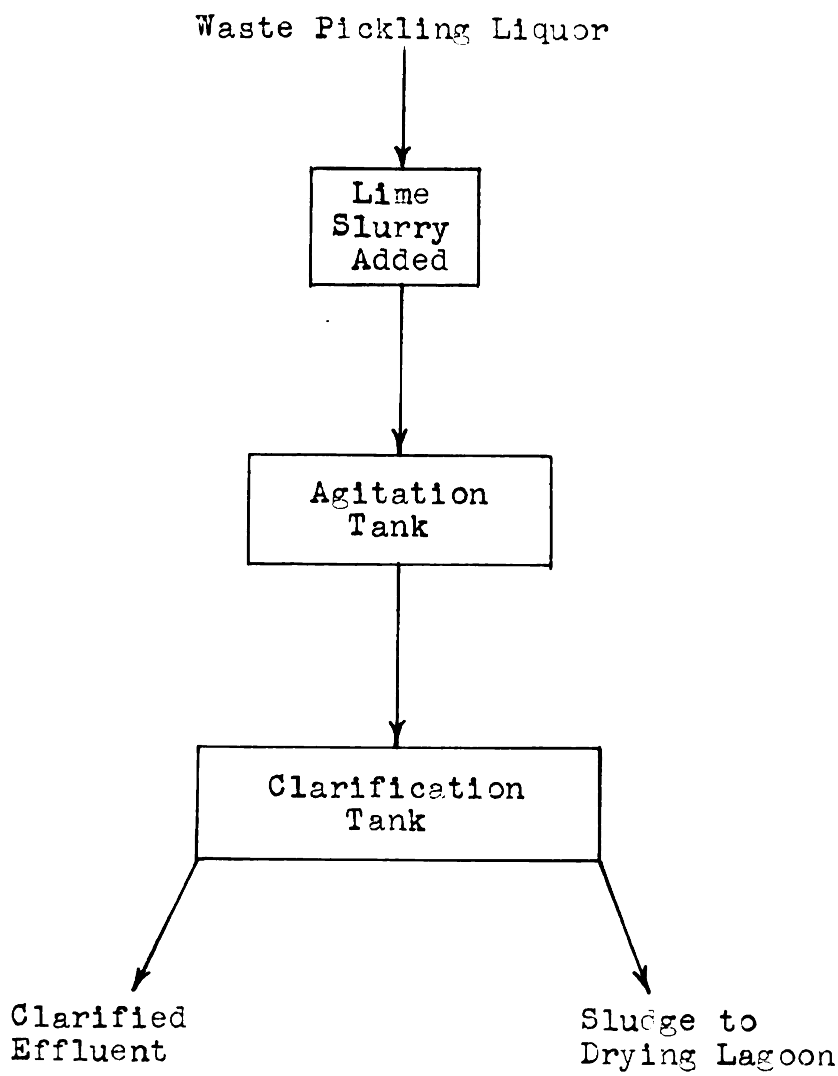
Limestone has been used for the treatment of the waste pickle liquor rather infrequently and with results which were not too successful. This was due to the method used which consisted of trickling the waste liquor through beds of lump limestone. The sulphuric acid reacted with the limestone to form calcium sulphate. The calcium sulphate formed a layer on the lump limestone which was quite impervious. This prevented a complete utilization of the limestone. However, when the limestone is pulverized, the process is much more effective since the fine particles tend to act more nearly to completion. All of the free acid is neutralized but not all of the iron is precipitated, because a high enough pH is not reached. Where oxygen can be supplied by aeration or otherwise, all of the iron can be removed. The reactivity of the limestone is dependent upon several factors. Some of these factors are the content of magnesium carbonate, crystal structure, fineness of pulverizing, and kind and amount of impurities. There is less sludge produced by the limestone treatment than by lime.

A process which has been developed, which when operated under favorable conditions, gives rise to a situation which could produce substantial savings. This is the limestone - lime split treatment. Pulverized limestone is used to neutralize the free acid and precipitate part of the iron. The treatment is completed by the use of quicklime. The operation of the process is started by the addition of pulverized limestone under rapid agitation. The limestone is added until the sludge has a light yellow color. This indicates that all of the free acid has been neutralized. No more limestone is added but the agitation is continued until a sample shows that evolution of gas has nearly stopped. Most of the carbon dioxide should be expelled to guard against its later reaction with the lime. Then, from a lime - slaking tank, milk of lime is added. Enough is used to finish the treatment at a pH of slightly above 9.

There are other alkalies which can be used to neutralize

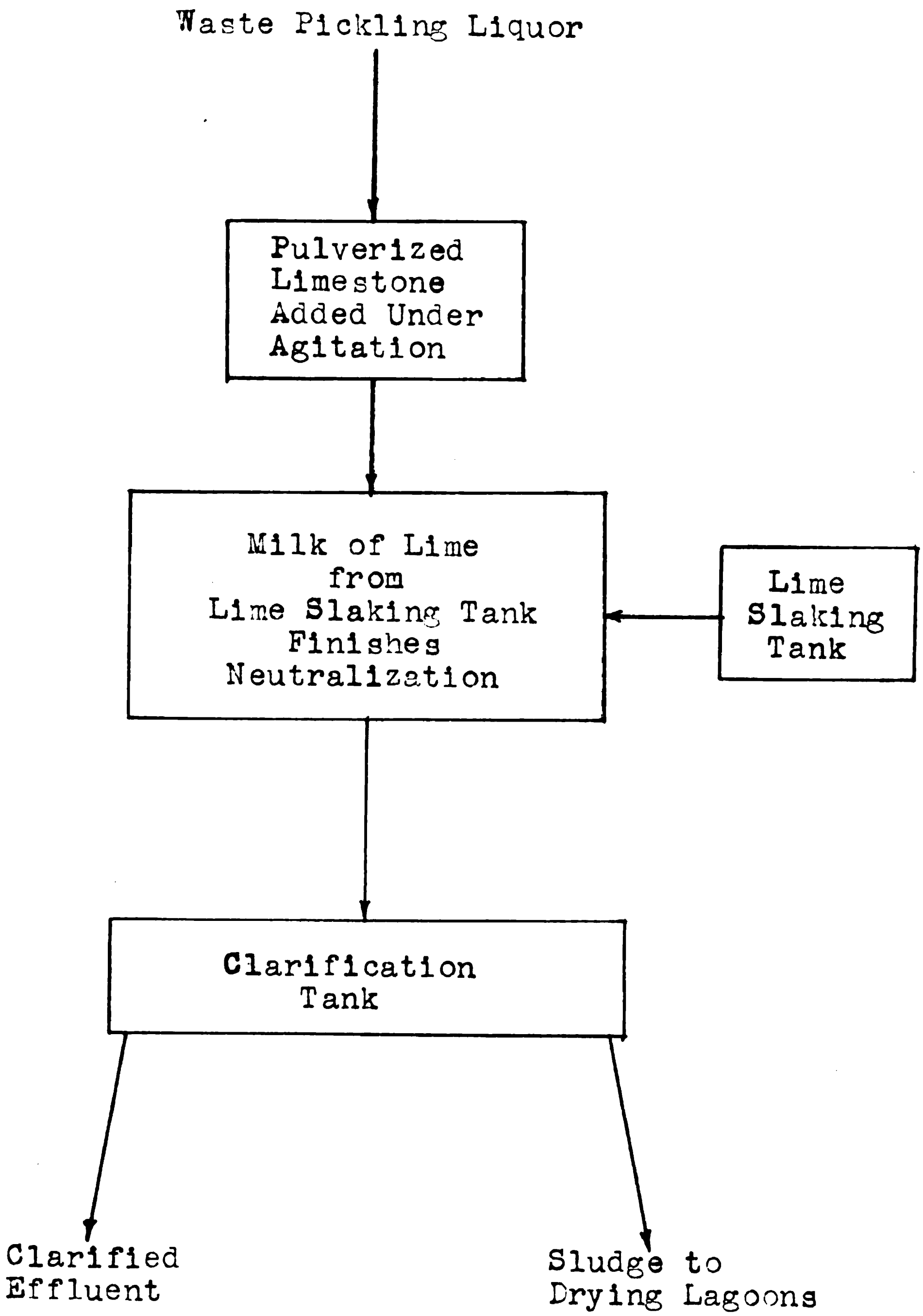
the waste pickling liquor. Also treatment has been made using ground basic slag. This treatment is not too successful, however. The reaction was not only slow but also rather incomplete. In some cases, objectionable quantities of hydrogen sulphide have been produced. From all of the neutralization processes the settled sludge must be disposed of. This is done usually by hauling it to a dump which should be situated so that heavy rains cannot wash any of the sludge into a stream or lake.

Flow-line Diagram of a Typical Lime Neutralization System



Flow-line Diagram Of Lime-Limestone

Split Treatment



EQUIPMENT

The equipment used in most of the utilization and neutralization processes is standard except in some of the utilization processes. However the air, sludge removal, and sludge drying equipment used in neutralization processes are standard stock with companies who manufacture sewage disposal equipment. The neutralizing tanks, however, should be of wood construction or lead lined to prevent action on them by the sulphuric acid. Lead lined or rubber lined pipe is used to carry the waste. In some cases, equipment is made with conduits and other parts manufactured of Monel metal because of its resistance to corrosion.

CONCLUSION

Shortage of time has prevented the accomplishment of a more comprehensive discussion of this problem. Some of the processes developed have been omitted along with some which are still in the experimental stage. Others which were discussed were done so with less extent than is desireable.

It is satisfying to know that this problem of treating spent pickling liquors is being met with solutions which are gradually cutting down its harmful effects and it is hoped that such progress will continue. Industrialists are spending large sums of money not only for treatment but also for research in developing new processes and techniques. Some have benefited by being able to employ a process which is an economic success. Others, while not being fortunate enough to show a profit from the treatment, have been able to show less loss by adopting a process which best suited the demands of the circumstances. Certainly, we have all gained by such treatment as has been used. Gains, such as better recreational facilities, more favorable water supplies and various other things connected with this problem. We have profited, if not by a betterment, then by a situation which is not made worse. In some cases, there is definitely a need for more education, especially of the interested layman and probably in isolated cases of certain industrialists. Sparkling clear streams teeming with fish are an impossibility in a highly industrialized era such as ours, but there are situations which are objectionable and should be remedied. It is hoped that these cases can soon be remedied by methods which can be operated at a profit or, if this is impossible, the smallest loss possible. It takes a long time to restore a body of water to a condition which makes it a suitable habitat for its naturally contained organisms and which makes it a satisfactory source of recreation and water supply but it can be changed from a condition which is satisfactory to one which is not in a very short time.

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BIBLIOGRAPHY

" Industrial Waste Treatment Practices" E. F. Eldridge

" Industrial Wastes and Fish Life" from "Proceedings of the First Industrial Waste Utilization Conference" M.M. Ellis

" Treatment of Wastes Produced in Metalurgical and Metal Working Industries" from Proceedings of the First Industrial Waste Utilization Conference" William S. Wise

" A Digest of Industrial Waste Treatment" Christian L. Siebert

" Sewage Treatment and Industrial Wastes" from "Proceedings of the First Industrial Waste Utilization Conference" D. Bloodgood

" Treatment of Spent Pickling Liquors with Limestone and Lime" Richard D. Hoak, C. J. Lewis, and W. W. Hodge from " Industrial and Engineering Chemistry", Vol. 37, June, 1945

" Waste Problems of the Iron and Steel Industries" W. W. Hodge from Industrial and Engineering Chemistry, Vol. 31, Nov. 1939

" Water Treatment and Purification" William J. Ryan

" Water Treatment" G. V. James