THE TREATMENT OF MILL EFFLUENTS

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The following paper was read by E. P. HEDLEY, Ph.D., M.I.Chem.E.:—

Two years ago Dr. Park Ross and Mr. L. de Froberville read before this Association a Report on an investigation of the methods used in Europe to deal with the effluents from distilleries and some Continental sugar factories. At the same meeting the present writer read a short paper embodying the results of experiments on the treatment of the effluent from sugar mills in this country and describing a simple plant which one mill was putting down as a result of this work, to treat its effluent waters.

The present paper constitutes a report on the waste waters from another mill where a plant was built on the lines laid down by the former two gentlemen and differed from that just referred to only in being continuous in operation. The waste waters which are treated by this plant are made up from the mill washings, floor washings and wash waters from the filter press cloths. As is well known, these latter are the most polluted and carry with them pieces of milo not removed from the cloth, as well as the cake in the cloth itself. If such water passed directly to the river a serious pollution would result. The removal of the colloids, gums, etc., which on fermentation would pollute the river is effected by precipitating the solids by rendering the alkaline waters still more alkaline and then adding alumina ferric.

A sketch of the plant used to effect this clarification is shown in Figure 1. A.B.C.D. are four tanks, 3,000 cubic feet in capacity, pyramidal in shape and closed at the bottom by a 3 inch cock. The waters to be treated are pumped, by means of a double ram Cameron pump of 9,000 gallons per hour capacity, into a gutter " E " which runs along the top of the tanks. At the end of this gutter, over tank D, the water is discharged into another gutter (F), which runs across D. Here the water discharges over the whole side of F, thus distributing the water evenly into D. On its way to D the water is treated at its point of entrance (G) with milk of lime, and further on in the gutter the mixture meets a block of alumina ferric, which is slowly dissolved by the passing waters. The lime and alumina ferric precipitate the gums, colloids, etc., and these are separated by the slow passages of the water through the tanks A, B, C and D. To assist in the precipitation, a vertical baffle, 2 feet deep and 2 feet from the end at which the water enters, is placed in each tank (shown at H in the broken section of C). The waters issue from the end of this train of tanks into the gutter I and flow away through the pipe K. The sludge resulting from the precipitation of the colloids is removed from the bodies by the cocks C1, C2, C3, C4, at regular intervals, and passes down the gutter L to a montejus (not shown) to filter-presses. The water coming from the presses passes away with the clarified water from the settling system.

The plant is not automatic in its operation. The water entering at G contains pieces of bagasse, burnt bagasse as smuts from the chimney, small pieces of sack, etc. These must be removed by passing through a wire mesh, 3/16in. holes, and this wire requires to be cleaned frequently otherwise the water will not pass the sieve, and therefor overflows and creates a nuisance on the ground below. If these solids are not taken out of the water in this way the piping feeding the filter-presses become clogged and the presses cease to function. The attendant is further occupied by releasing the sludge from the bottom of the bodies.

This is a description of the plant used to sediment the solids in the wash waters. Now let us consider the results.

THE WASH WATERS.

In the paper referred to above by Dr. Park Ross and Mr. de Froberville, the authors state that at Froyères milk of lime was used to maintain an alkalinity between 0.6 and 1.0 parts per litre. To this figure we worked, but it was found necessary to add more alumina ferric than the ferrous sulphate used at Froyères. Alumina ferric to the extent of 1 part in 500 of water gave the best precipitation. Most of the settling took place in the body D, a little in C, usually none in B, and never any in A. This was due to the fact that the plant never had to deal with its maximum capacity. Each body can hold 3,000 gallons, and it was a rare thing that the plant had to deal with more than 3,000 gallons per hour. The water passes into the plant as a thick muddy effluent and leaves the plant as a clear yellow liquid without smell and with a strongly alkaline reaction. Its further course will be explained later. Much of the mud in suspension would settle out without treatment with lime and alumina ferric, and I am of the opinion that it would be preferable to allow this to take place in body D, then collect the overflow and treat it with lime and alumina ferric. This would certainly effect a saving in chemicals and produce just as useful a result. From my experiments carried out during the year I can safely say that so far as this plant is concerned the emphatic statement by Dr. Park Ross that "the lime must be kept between 0.6 and 1.0 parts per litre" does not apply. Less will do, if the mud is first settled, and less alumina ferric also. The clarified waters, of course, always contain sugar, which ranges between 0.5 per cent. to 1.5 per cent.

Effect of Storage on the Wash Waters.

As is well known, if these unclarified waters are stored in dams they ferment rapidly and become an intolerable nuisance. The give rise to large volumes of sulphuretted hydrogen, particularly on a hot day. The water blackens and, finally, after months, they settle to a quiescent state. Again if the clarified water is kept, the alkalinity decreases, due to the lime being precipitated by the carbon dioxide of the atmosphere, fermentation sets in, the mass becomes acid up to a certain point, and then the acid value falls until the liquid is nearly neutral. During fermentation butryic acid is certainly formed, and at the end of the fermentation the disgusting smell of butryic acid is greatly reduced and esters seem to take its place. The acid and esters were not isolated. These changes are shown in Fig. 2; A, B, C were three different volumes of clarified water, A being 400 c.c., B 800 c.c. and C two litres. The surfaces exposed to the atmosphere were identical in each case. It will be noticed that the greater the volume of liquid fermenting the slower it took to reach the end point, which was only to be expected.

After these experiments were concluded there appeared in the I.S. Journal, November, 1929, a paper by Wallace Montgomery, who had been studying the waste waters from Beet Sugar Factories, and he found that a similar change takes place with silo drainage water and pulp water.

If instead of keeping the clarified water alkaline as it comes from the settling plant, it is made acid at once—the water will keep for weeks without undergoing any change.

Again, if the clarified water is diluted with water 1 in 100 and kept, fermentation in most cases is delayed, but starts eventually giving rise to sulphuretted hydrogen. In other instances nothing happens apparently.

All these observations are of value because the clarified water passes eventually into the river, being diluted with the condenser water.

THE RIVER WATERS.

In order to determine the extent to which the factory affects the river the waters were examined at three points. It should first be pointed out that the factory draws its boiler water from a dam across the river above the factory. Just below the factory another dam is built, and the water between the dams is used for the condensers of the pans and the multiple evaporator. This condenser water passes along a flume to a cooling tower and thence to the river between the dams. This process is repeated day and night, the water therefore being continually in circulation.

The river, however, is flowing continually over both dams. Below the second dam a part of the condenser water is discharged continually. It is in this water that the clarified water from the settling plant is returned to the river.

The river water above the first dam, so far as factory pollution is concerned, is of course satisfactory. The analysis of several samples are given below.

The circulation water between the two dams at times smells of sulphuretted hydrogen and shows a high oxygen absorption figure especially towards the end of a week's work. It is difficult to see where the sulphuretted hydrogen comes from as no milo drainage or the cake itself can enter the river between the dams. The oxygen absorption figure can be explained when it is remembered that nitrogen compounds are carried away in the condenser water, the pH. of which is always about 7.2.

The water below the dam is clearly polluted to a certain extent since the clarified water from the settling tanks enters the river here.

The analyses of these four waters are as follows, and for comparison that of the River Ouse, on which is a Beet Factory, is given.

	Solids in parts. per 100,000.	Ash parts. per 100,000.	Oxygen Absorption from N/80 $KMnO_4$	
			15 Min.	4 Hours.
Pure River Water	20 to 30	14 to 18	—	4.14 to 0.63
Circulation Water	22 to 31	16.18	.21 to 3.7	0.61 to 6.4
By-pass Water	30 to 40.6	17.6	.6 to 4.3	1.6 to 8.2
Below Second Dam	22 to 34	17 to 18.5	.30 to 3.9	.80 to 7.0
Clarified Water	2049 to 2400	200 to 272	400	1000
The Ouse above Factory	23 to 38	10 to 20	—	0.12 to 0.77
The Ouse below Factory	24 to 38	11 to 25	—	.14 to 0.61

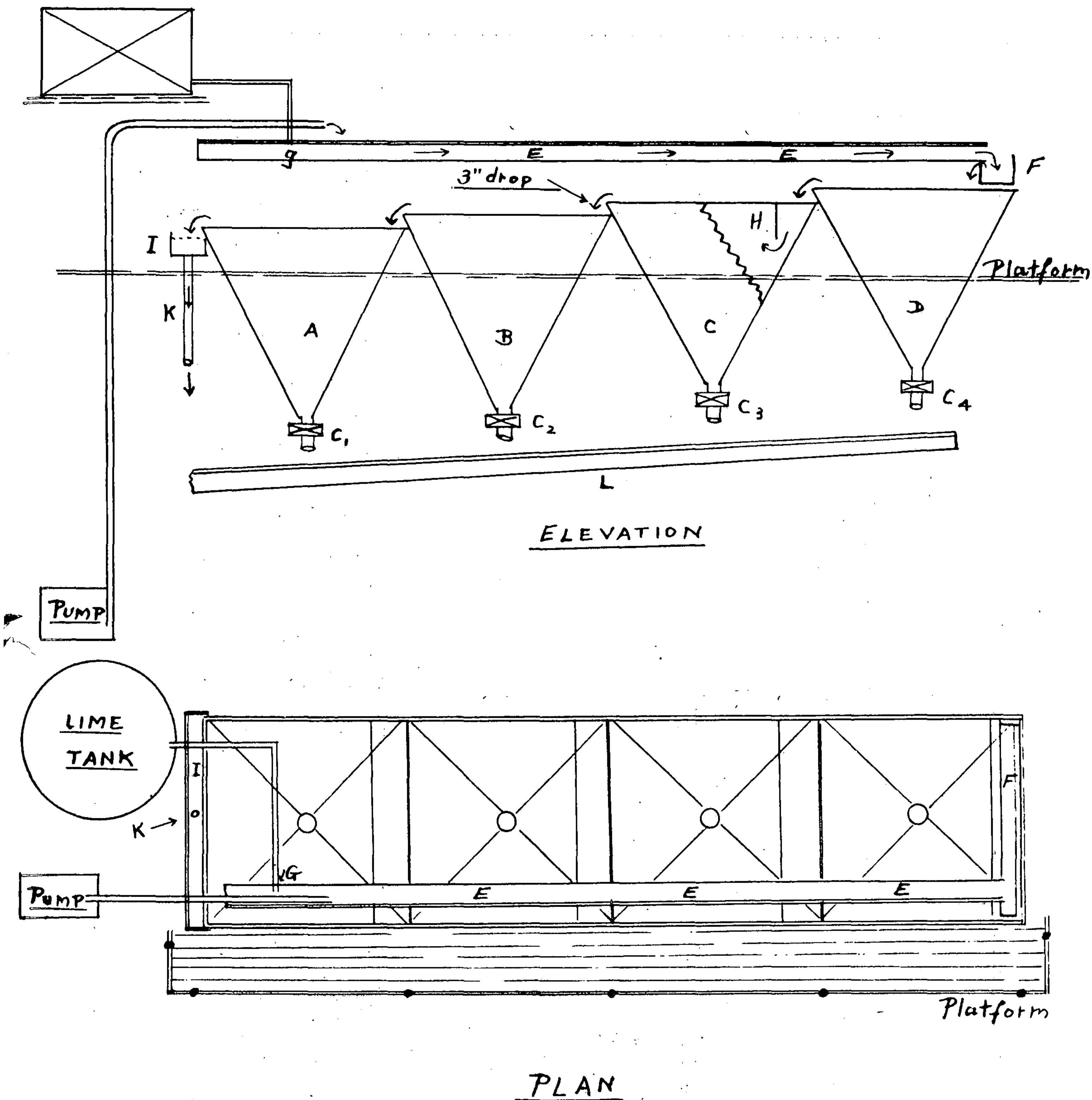
g
E
E
F
3" drop
H
I
K
A
B
C
D
Platform
C1
C2
C3
C4
L
ELEVATION
Pump
LIME TANK
I
K
G
E
E
E
F
Pump
Platform
PLAN

FIG 1.

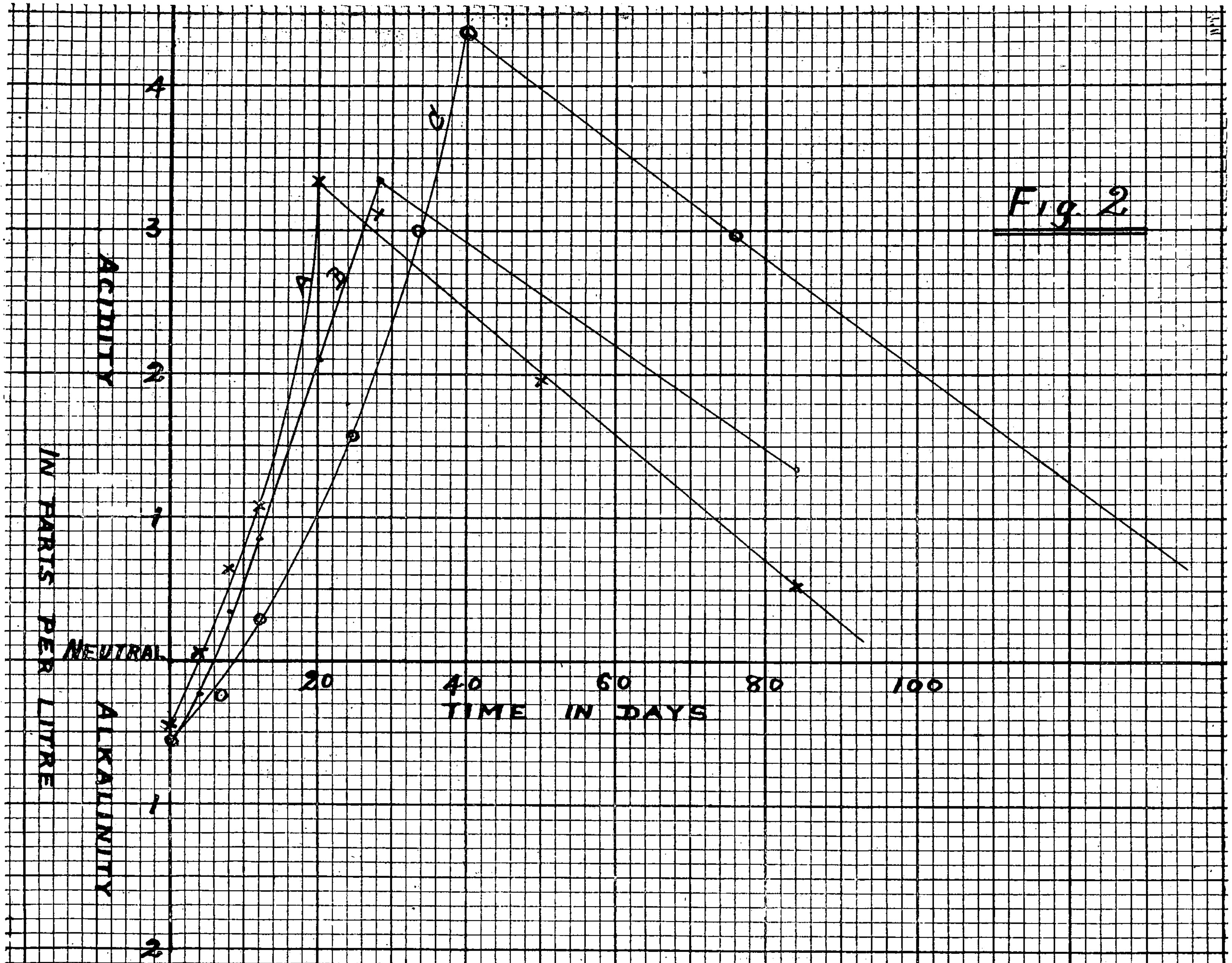
ACIDITY
IN PARTS PER LITRE
ALKALINITY
NEUTRAL
TIME IN DAYS
4
3
2
1
1
2
20
40
60
80
100
A
B
C

Fig. 2

In the river tank it will be seen that normally the solids and oxygen absorption compare very well with the figures shown by the Ouse.

In the circulation water the solids rise a little, but the oxygen absorption shows that the river is polluted, the lower figures being obtained after the river has been flushed by rain. Other signs of pollution in the river itself are to be found in the growth of fungi on the rocks, dam walls, etc.

The by-pass water is that portion of the condenser water which passes to the river below the second dam and contains the whole of the clarified water. The dilution of the latter is about 1 in 100. This by-pass water, as is therefore to be expected, contains more solids than the circulation water, and the oxygen absorption is greater, the lower figures being given when no clarified effluent is being conveyed by it. The pH. is about 7.1.

Those figures given by the water below the second dam show the effects of further dilution, but not much improvement in oxygen absorption. This, too, would be expected when it is remembered that the diluting water (the circulation water, which overflows the second dam) also shows a high oxygen absorption value, and but little solid content. The river itself shows the effects of impure water by the fungi on the rocks, its colour and its smell. The latter while not objectionable is characteristic.

We now come to the clarified water. The solids are very high and the ash very much lower than the solids. The solids consist of sugar, glucose and other organic compounds chiefly together with free lime and lime salts, such as phosphates, sulphites and bisulphites, potash and magnesia salts. A complete quantitative analysis was not done. Owing to the presence of the sulphur compounds especially, the " oxygen absorption " shown is enormous, but as stated above this figure is greatly reduced in the river by dilution with the condenser water and again by the dilution of the latter with the river water itself.

In order to see whether further treatment would improve the circulation and by-pass water, they were both rendered alkaline and alumina ferric added. There resulted in both cases a water white liquid, but on keeping both the unclarified and the clarified waters developed sulphuretted hydrogen. Like all the experiments recorded, this operation was repeated many times and always with the same result. A typical experiment gave the following:—

Date.	BY-PASS WATER. Oxygen Absorption per 100,000 in N/80 $KMnO_4$ After Four Hours.		CIRCULATION WATER. Oxygen Absorption per 100,000 in N/80 $KMnO_4$ After Four Hours.	
	Clarified.	Unclarified.	Clarified.	Unclarified.
21/11/29.	8.19	8.43	4.17	5.96
6/12/29.	11.39	10.80	4.84	8.18

The increase in oxygen absorption is undoubtedly due to the decomposition of sulphur compounds by bacteria, for at the beginning of the experiment none of the four waters smelt of sulphuretted hydrogen, but as time went on the smell of the gas became more and more pronounced.

It seemed of interest to see whether the bacterial concentration was very great, and the Union Health Laboratory at Durban very kindly carried out the assay.

Four waters were examined—(1) the river above the first dam, (2) the circulation water, (3) the by-pass water, and (4) the clarified water from the purification plant.

The report shows that in (1) on nutrient sugar the total number of organisms was 100, in (2) this number has grown to 800,000,000, B. Lactis Aerogenes and B. Alcatigenes constituting the greater portion of bacillary forms, in (3) the number was so great that it could not be counted, and in (4) only about 400 were present.

It is therefore very clear why the two waters in the above table should, on keeping, get worse instead of better.

The problem of dealing with mill effluent waters before us in South Africa is a very different one to that of dealing with beet factories' effluent. Those beet factories which work the Raabe continuous diffusion process have overcome their problem of the disposal of the most troublesome effluent by using this process, for in this process there is no diffusion water to get rid of, their other waste waters being purified by lime and settling ponds, and the condition of the Ouse shows the success met with. Those beet factories using discontinuous diffusion have had a serious and difficult problem to face, but overcame it by promoting lactic acid fermentation of the diffusion water in special ponds. They were able to do this because the effluent from the diffusers is hot, and when kept hot, 40°—45° C., lactic acid fermentation sets in. In South Africa I do not see at present we can produce by fermentation or any other means a water white effluent, the oxygen coefficient of which will compare well with the river. Lactic acid fermentation is out of the question for us, because the waters which we have to deal with are cold, and most factories have no surplus heat available to raise the temperature of these wastes. If the unsettled water ferments spontaneously there results an intolerable volume and smell of sulphuretted hydrogen, which is a public nuisance; and if the clarified water spontaneously ferments, the smell of butryic acid, etc., resulting is almost equally objectionable.

If the waters are not fermented, but merely settled, as is done by the plant described in this paper, there is bound to be pollution in the river to some extent. Perhaps the solution will come from a different source, e.g., the winning of a different type of filter cake such as the experiments with Oliver filters indicate might be obtained.

In any case it cannot be denied that considerable progress has already been made, and better results must be left to future investigation.

CHAIRMAN: This is a most interesting and important paper. I am only sorry that Dr. Park Ross, of the Public Health Department, is not here to discuss it with us. It shows that a lot of work has been done on this very difficult problem of the disposal of waste waters and that a good deal remains to be done before the problem can be regarded as satisfactorily and finally solved.

Mr. DYMOND: As Dr. Hedley has rightly pointed out the main difficulty in the treatment of effluents is the getting rid of the fermentable portions which are in solution. It is merely a mechanical problem to get rid of the suspended matter, which does not help the problem at all. As he points out, the fermentation by lactic acid bacteria would destroy the sugar in solution, and the precipitated calcium lactate would be embodied in the surrounding total precipitation. He says, however, that this cannot be done owing to the waters being cold. Cannot this be overcome by the withdrawal of some portion of the circulation water, which in many factories is very high in temperature? It depends, of course, a good deal on the quantity of effluent to be treated; the waters from washing the presses, etc., are fairly cold, but a certain amount of the circulation water would bring up the temperature sufficiently for lactic fermentation, and that to my mind is the only way to solve this problem. Complete fermentation must occur before any additional lime is used, otherwise a fermentable body will always be present in the effluent.

Dr. HEDLEY: I think that is the only possible way of getting temperature. I think the dilution would be too great though. You will get free heat in that. In taking the samples I frequently burnt my hand; it was quite hot enough. But I think the dilution is too great. It would have to be kept in lagged vessels. The way they do it at Home is to dig ponds—they are enormous ponds, far bigger than the area of the factory and the yard. But they are very carefully worked out for capacity and depth. I noticed from the Institute of Chemical Engineers in a paper by Dr. Sprengler, that if they varied the size of those ponds by 5 per cent. they did not produce the results, and they were very specific about the dilution. As you know, the mills are not very well situated in the way of chemicals and apparatus, and when it comes to practical work the possibilities are non-existent. I simply had to allow the things to take the course of nature. There is no possibility of controlling them by thermostats and that sort of thing. But it is a thing that might be done; it is the only possible solution so far as I can see. I am afraid the dilution is rather too great to keep that quantity of water at 45.

Mr. BIJOUX: Could not that be done by using the hot condensed water from the evaporators?

Mr. DYMOND: Perhaps the difficulty might be overcome by using flue gases. I quite appreciate the fact that dilution would hinder fermentation very considerably, but the natural wild fermentation in this country is almost always followed by a secondary lactic acid fermentation. The use of flue gases is surely not an insuperable difficulty, while by the simple method of natural fermentation, and subsequent addition of lime, the fermentable matter would be precipitated as calcium lactate or butyrate.

Dr. HEDLEY: You might do it by flue gases. I must confess I never thought about them as I was never really asked to remove them. I don't think you would leave it to natural fermentation. What they do in Germany and England is to prepare a culture and inoculate these waters at once with these cultures so as to make up the period before the fermentation sets in.

Mr. POUGNET: You apparently destroy the alkalinity of the waters first.

Dr. HEDLEY: No.

Mr. BIJOUX: We have also had experience with the treatment and analysis of waste waters. The greatest difficulty lies, we believe, in removing the sugar, which it contains and is in far greater quantities than Dr. Park Ross allows to be left in the mill effluents discharged after the treatment in the rivers.

Dr. HEDLEY: Fermentation will remove the sugar; it takes place in the river. I have found the fish drunk in the river. I am not exaggerating in the least. The river sometimes gets low, the sugar concentrates, it ferments, and there is sufficient there for that to happen.

Mr. RAULT: Regarding the rate of deterioration of sugar, we have had occasion to test the sugar content of very dilute and impure solutions similar to the mill effluents, namely, the cooling water used for condensing the evaporator and pan vapours. This water contained a fair amount of sugar due to juice entrained in the boiling process. As it was kept in circulation for a whole season, we were able to test it day by day, especially when the mill was not crushing and when no new sugar was added to the amount already present. We were surprised to find that after two weeks no sign of decrease in the polariscope test was shown, and also that even after two months the presence of sugar could still be detected by the polariscope. It is true that lime was added from time to time to this water, but, nevertheless, it is apparent that decomposition of sugar in dilute solutions by simple exposure is a very slow process requiring a large plant.

Dr. HEDLEY: They say they have to keep it three to four months at Froyeres and other places on the Continent; therefore the necessity for a culture in order to accelerate the fermentation.

CHAIRMAN: I notice that the settled waters developed butyric acid in fermentation which eventually passed off. Could that be accelerated by the application of liquors containing waste alcohol?

Dr. HEDLEY: I think the way to initiate and hurry on fermentation would be to have a pure culture.

CHAIRMAN: The quantity of butyric acid actually there must be very small.

Dr. HEDLEY: It goes up on the curves to about 4 grms. per litre. It depends on the sugar content and the condition of whatever else is there fermenting.

Mr. BLACKLOCK: Some two years ago I did some experiments with Mr. de Froberville, and the result was the installation of a plant at the Refinery for dealing with the effluent waters. It was on the same lines as the plant which Dr. Hedley has described, and our experience there is confirmed practically by Dr. Hedley with his plant. We have settling tanks, and the water is treated by adding lime at the Refinery. The mixture goes from the Refinery to the settling tanks, which are about 600 yards away, through a 9-inch pipe, and during the journey thorough and intimate mixing occurs. The precipitation is excellent and the settling is very good indeed, and we produce a water-white effluent from the tank overflow which contains very little floc with it, but it leaves very much to be desired with regard to the standard of effluent. The oxygen absorption test is misleading and useless owing to, as Dr. Hedley says, the SO_2 and sulphites, or sulphides, present, and also on account of the traces of sugar remaining in the water. The figures range sometimes up to 20 or 29 parts per 100,000; that is above the standard permissible in reference to a test period of four hours. This water is clear and practically colourless and will keep as long as it is alkaline—over a month—without deterioration. Ultimately fermentation sets in, the alkalinity is gradually neutralised by the CO_2 absorption. The reaction becomes acid—H_2S is driven off from reduced sulphites and sulphates, and, added to this, there is the unpleasant odour of butyric acid. I have tested the water in the river above the point of entry and below and I can't say I found very much deterioration in the water in the river due to the entry of our waters. The oxygen absorption figure shows slight increase. Taken 20 yards above was .44 parts per 100,000 and taken 20 yards below the entry was .49 parts—on a four hours' test. The temperature of the water in the river before the entry of the effluent was 80° F. and after the entry 82°. The high temperature of our effluent water facilitates precipitation and sedimentation. Our water comes down from the Refinery round about 180° F.; by the time it gets through the settling tanks it is down to 140°, and by the time it reaches the river perhaps 110°. So that all the time it is hot. With regard to lactic acid fermentation I did not find any while any sample was settling; when it got to 45 degrees no lactic acid fermentation set in. We tried to improve the effluent water by aerating it, but it had the opposite effect. We also tried filtration through sand, but that was disastrous, too, because it seems the alkalinity is rapidly destroyed, acidity is developed, bacteria present in the sand act on the sulphates and sulphur compounds—sulphides are produced—H_2S driven off—black iron sulphide precipitated, and the result was a water more evil smelling and noxious than the original effluent. Dr. Park Ross wished us to filter through sand but we found it most unsatisfactory and disappointing as I have said.

Dr. HEDLEY: I am very glad to hear that Mr. Blacklock confirms my experience. One is always pleased to find that one is not standing by oneself. His oxygen absorption figures are much better, and the reason is simply that we discharge into a very small river—I think the smallest river on which there is a sugar mill. Mr. Blacklock discharges into a river with a much greater flow than the Nonoti, consequently his dilution factor must be much greater. That accounts for his finding practically the same amount below and above the entry. The temperature of his effluent waters would greatly assist in settling. Ours being cold sometimes it settles away into the third tank before the very fine floc disappears. The colour of his water is water-white and ours is almost always yellow. He is dealing with a better material and he has not the dirty stuff we have in the raw sugar.

Mr. BECHARD: The question seems to me to boil down not to a mechanical question but to a question of the fermentable matter in the water which can surely be dissolved by some form of fermentation. Dr. Hedley suggested lactic fermentation; that is very useful in the Old Country, but under the conditions we have here probably another form would be very useful. We have a very hardy form which has lately been investigated in Cuba. This is exceedingly resistant; I have had this under the microscope and it is very difficult to destroy. It is not quite clear what its products are. It grows very fast, but it is a question to find out what its products are. I have not found any evidence of objectionable smell. But then I have not had the culture in sludge. It is surely a question for a bacteriologist. I should say it is possible to evolve some form of fermentation that would be suitable for the climate in this country.

(At 12.55 p.m. adjourned to 2.30.)

On resuming at 2.30 Paper No. 9 was taken.