Report on Waste Waters.

By J. C. R. Bijoux.

Waste waters come under several classes, and their composition and treatment vary accordingly. Those coming from factories are called industrial, as against drainage, sewerage, and other kinds of waste waters. Waste Waters are complex mixtures of unstable composition, which varies every day, and at every hour, thus rendering difficult their purification. Such waters contain generally organic matter in suspension, colloidal solution, and in solution, as well as a high percentage of ammonia. It is owing to the presence of organic matter that waste waters are offensive, because it becomes decomposed under the influence of micro-organisms, with the production of evil-smelling substances. If, therefore, all the organic matter could be completely removed from these waters, they would become absolutely harmless, so far as decomposition is concerned, and this can be attained by either chemical, physical or biological means. It is most important, whatever be the method of treatment adopted, that the concentration, and as much as possible, the chemical composition of such waters, be made constant, in order to ensure the best results, and, as the aim of the treatment is to destroy fermentation, it is essential that the floating impurities be first removed to minimise difficulties during the treatment of the waters themselves. There are several processes by which waste water can be purified: *i.e.*, by decantation, entrainment or precipitation, electricity, oxidation, or by biological means.

The Decantation Process:

The decantation process is a long one, and liable to the risk of decomposition of the waters taking place if the suspended matters are allowed to accumulate in their presence. This not only imparts a bad smell to them; but is likely also to produce an increasing amount of colloidal organic matter, which can be removed only with great difficulty afterwards, as it cannot be precipitated.

The Entrainment Process:

Based on the property that such waters have, of being electrically charged, they are often mixed with negatively charged substances such as ferric alumina and lime, which permits the entrainment of their colloidal matters to the bottom of the dams where the settling takes place.

The Precipitation Process:

Sulphur dioxide coagulates suspended organic matter, and is sometimes used in this connection.

Electricity:

This acts in the same way as sulphur dioxide.

Oxidation Process:

It is only by oxidation that the soluble colloidal organic matters can be removed, and this is done by alumina in presence of the oxygen of the air, for alumina thus (a hardly known fact) acts as a catalyser. Ammonia is also removed by oxidation. The oxidation of organic matters can also be obtained by biological means, which, contrary to the use of chemicals for the attainment of the same results, are less expensive, and have the advantages of receiving the aid of Nature. If, however, industrial waste waters contain products prejudicial to biological treatments, they can only be purified by chemicals means.

Beside the pre-mentioned methods of purification, a new technique has just come to light, which is an improvement on already known biological processes called the treatment by activated mud.

Biological Processes:-

The process of treatment by Activated Mud is based on Schloesing's theory of dissociation by means of micro-organisms and the oxidation of ammonia to form nitrates. Activated muds, in as short, a time as five minutes do what the soil, septic and percolation beds do in days and months. The application of this method has found great favour in England, America, Belgium and France. Industrial waste waters have been successfully treated by this method, which, at first, was thought only suitable for sewerage and drainage waters. It is thus that breweries, dairies, and sugar factories are now treating their waste waters in these countries.

The Preparation of Activated Muds:

We owe this discovery to Ed. Arden and W. Lockett. This mud is obtained by accumulating drainage mud, and aerating by a strong air current until it acquires the property of oxidizing into the nitric-nitrogen form, ammonia and soluble matters, and of absorbing colloidal ones. It differs totally in appearance to sewerage muds, being a precipitate of a colloidal aspect, and when dried has a smell of humus, quite different to that of suspended muds of sewerage origin, which have such a characteristically offensive one. When seen under the microscope, activated mud appears as an amorphous precipitate similar in appearance to a precipitate of ferric oxide or alumina, containing numerous microbes, particularly a kind of monad which is present in all prepared activated muds, whereas sewerage muds contain vegetable and animal cells, still full of protoplasm. Pit soil, and humus from garden soil can also be transformed into activated muds. In practice, the aeration of the mud is done together with its accumulation. The operation is as follows: The waste waters, rid of their heavy particles of sand, straws, etc., are introduced into a reservoir where the aeration is carried out at the rate of 200-250 cubic feet of air to 30 cubic feet of water. The air is then shut off, the mud allowed to settle, and ¾ of the supernatant liquid decanted off. The reservoir is again filled, and the process repeated until at the end of the aeration, nitric-nitrogen appears whilst the ammonia disappears. This takes place suddenly. All waters are capable of producing activated muds. If, however, there is no sediment to act as a support to the nitrifying germs, this can be remedied by adding chalk, clay, ferrous sulphide, or any other suitable porous material to that effect.

Mud prepared in such a way can nitrify 20 mgs. of ammonia per litre of water per hour. The best results are attained by the use of mineral activated muds, which are five times as active as the organic muds and have the advantage of being more quickly prepared. The less there are present of organic matters in the water, the more active can be the mud. The addition of lime, ferrous sulphide, petrol and manganese dioxide hasten nitric fermentation, and procures the most active kinds of muds, as Dr. Cambier found by experiment. As soon as nitric-nitrogen appears in a mud in activation, in less than a week it acquires its maximum power of activity, which is governed by weight of accumulated mud and temperature.

The Process of Purification by Means of Activated Muds:

This process of purification of waste waters consists in placing the prepared activated muds in reservoirs or dams, where they are put in contact with the water by means of diffused air passing through slab filters situated at the lower doors of these dams. The characteristic of this process is the grouping together of the four identical dams where succeed automatically the filling, the blowing, the settling and the emptying Sedimentation and oxidation are accelerated by the use of certain catalysers. The following results were obtained in using this process to purify distillery and sugar factory waste waters in Belgium and in France.

RESULTS OBTAINED IN THE TREATMENT OF DISTILLERY AND SUGAR FACTORY WASTE WATERS BY THE ACTIVATED MUD METHOD.

D. 1. Distillery Waste Water:

	Before Treatment.	After Treatment.
Reaction	Neutral	Alkaline 218 mgs/litre.
Ammonia	12 mgs/litre	Traces.
Nitrates	Nil	Traces.
Nitrites	Traces	Slight Traces.
Coloration	Blackish	Limpid.
Smell	Nauseating	Nil.
Organic Matter in terms of oxygen	Nil	Nil.
Observations	Fair amount of suspended matter.	Nil.

S. F. 4. Sugar Factory Waste Water:

Reaction	......	......
Ammonia	5 mgs/litre	Strong traces.
Nitrites	Traces	Fair amount.
Coloration	Deep Yellow	Whitish.
Smell	Nauseating	Nearly Odourless.
Organic Matter. in terms of oxygen	296 mgs/litre	136 mgs/litre.
Suspended matter.	Nil.	Nil.

S. F. 3. Sugar Factory Waste Water:

Ammonia	4 mgs/litre	.6 mgs/litre.
Nitrites	Nil	Nil.
Coloration	Yellowish	Whitish.
Smell	Slight	Nil.
Organic Matter in terms of Oxygen	266 mgs/litre	96 mgs/litre.
Suspended matter.	Nil	Nil.

S. F. 2. Sugar Factory Waste Water:

Ammonia	32 mgs/litre	4 mgs/litre.
Nitrites	Present in strong traces.	Fair amount.
Coloration	Deep Yellow	Limpid.
Smell	Nauseating	Slight.
Organic matter in terms of Oxygen	471 mgs/litre	322 mgs/litre.
Observations	No suspended matter.	No suspended matter.

Total decantation was obtained and the time of treatment was 1½ hours. Although these waters fulfilled the conditions required by the sanitary regulations and could be discharged into the rivers, yet, their treatment was not considered complete as the equilibrium between waters in treatment and treated waters had not been reached. This was obviously due to the waters having only been treated once by the batteries.

Experiments carried with wash, diffusion and press waters lead to the following conclusions: That wash waters must necessarily before their passage into the purification dams, be decanted owing to their high content of solid matter. That, the average flow made of decanted wash waters and the water from the presses can be purified by the activated mud process.

The waters flowing from the dams after treatment had the following properties: Absence of ammonia tested with Nessler's reagent, absence of sucrose, and complete deodorization. These results are sufficiently convincing to demonstrate that the activated mud process has brought to the sugar factories' waste waters purification problem the most elegant and economical solution yet offered. It is now possible to combine both economy and sanitation. We are glad to call the attention of the Association to such a solution which appeals both to efficiency and low running cost. Following these results Batteries under new dispositions are now working at: Sheffield, Manchester, Milwaukee, Houston, Cleveland, Court (Belgium), Roubaix, Tourcoing (France), etc. Adopted by the Sugar Syndicate of France.

(Notes extracted from the Engineer's Review of France, and experiments described, and carried out by Technicians of the A.C.E.N.I. Society in Paris under the supervision of Mr. Dienert, Chief Engineer in charge of the City of Paris.—Published in, and translated and arranged from the *La Revue Agricole de l'Ile. Maurice*)..

The Chairman said that this process mentioned by Mr. Bijoux seemed to offer great possibilities, and he was sure that the members of the Association would be willing to put it to the test.

Dr. Park Ross asked whether he might make a suggestion. Certain of the remarks that had been made appeared to advocate a precipitation process. Mr. Bijoux who had just spoken had put a very strong plea for activated seudge. There were one or two activated sludge plants working in South Africa in connection with sewerage; but he must confess it was absolute news to him that a similar process had been actually working in regard to sugar. He did not know, however that it was of any use in any of the distilleries, because as far he remembered, according to the Royal Commission's report, on the Speyside they went in for a biological process, which involved a tremendous amount of water, and he, personally, had hesitated recommending any of the sugar mills to try the biological process on account of the tremendous amount of water required. If he remembered rightly, it was, for distilleries, nineteen times the amount of water for the amount of wash they were going to treat. He remembered that one of his colleagues in the health line in Durban attempted to press the biological purification of sugar effluents at South Coast Junction at one time, but as the factories in question were buying water from the Durban Corporation at a pretty high cost, he thought it better to stand out of the matter. Consequently they did not take it up. He would like to hear whether the gentlemen concerned would be prepared to recommend to the mills a trial in connection with precipitation by lime, or any other chemical; or, on the other hand, a trial by the activated sludge method. It seemed to him that this was a question which affected all the mills. Some of them were specially well placed for trying the one process, and some for trying the others. He noticed that Mr. Bijoux came from Amatikulu—Mr. Warner was looking very interestedly at him (the speaker); they had a tremendous amount of mud at Amatikulu. He thought it would be a very good scheme.

There were other mills, of course,—he was trying to pick out one not of the Hulett group—where he thought they might hear the chemists speak on the process. He put it to them that it was a fair thing that the industry should start immediately by giving both processes a good experimental trial, and let them see where they were. He certainly as an officer of the Health Department would like to hear of a move in both directions. He could not talk technically on the actual treatment of those things, but his suggestion was that they should hear a discussion now as to what the possibilities were, and what the costs would be of working on the one hand, by precipitation and, on the other, by activated mud.

Mr. Blewett said it was one thing for Dr. Park Ross to talk about the manurial values of some of these wastes. The matter was complicated in this way, that those materials consisted of small percentages of plant food such as nitrogen, potash, etc., and a large amount of organic matter. Organic matter nobody bought at all. It was undoubtedly of tremendous value and they would undoubtedly hear more of it in the near future, now that experiments were being carried out by Mr. Dodds. Organic matter was never paid for by the farmer when he bought fertilizer. The Fertilizer Act laid down that a fertiliser sold as a mixed fertiliser, must contain 12 units of plant food. If they were to put on the market this product from distillery waste liquor which could be obtained by precipitating with lime, it would be a violation of the Fertiliser Act. On the other hand, they knew what little value the planter placed on organic matter, which he got for nothing or next to nothing; if he got it for nothing he looked upon it as being of no value at all. As far as his (the speaker's) observation was concerned, a very large proportion of organic matter available to-day was wasted. Until they had more reliable informaction as to the return that could be obtained with cane by returning organic matter to the soil, it was not altogether wise to tell a planter that he could afford to pay a certain sum of money per ton for this dry residue. What he wants to know is, what return he will get per ton used.

One other difficulty in the way was this: supposing a fertilising firm bought this material, which contained about 1.8% nitrogen, and contained a large amount of lime. It was quite true that lime was very useful on cane lands, but if this material was bought by fertiliser firms it made water soluble phosphates less soluble, a complication which arose if they were selling mixed fertilisers. He merely mentioned those points to show that it was not so easy as it looked to get the full value that was really there in much organic waste. Ultimately all that stuff would be used; whereas to-day it was a nuisance, it could become a real valuable addition to the soil.

The Chairman remarked that according to what Mr. Blewett had said, those things would never be chemical fertilisers, but they would certainly be very valuable organic manure. Organic manure to old planters and those who were very keen on getting good results, was certainly extremely valuable. There was no doubt that the old planters, whose soils had been under cane for forty and fifty years, found today they could not obtain results without fertilisers, and in places on the North Coast such as Tongaat and Mount Edgecombe, the planters were very keen on obtaining all the fertiliser they could get on the estate. They took all the refuse, filter press cake, and whatever they could get for organic manure. They were very pleased to secure such. In Zululand, to his surprise, no one wanted to buy it. Having been born and bred practically on sugar estates, and knowing what the conditions were, he was very shocked to find that in the Huletts' group the very valuable filter press cake instead of being bought by their own planters was sent to the other side of Mount Edgecombe. The planters apparently did not want it; but they would eventually want it. They would have to start this business of purifying the waste water, which would certainly be of some expense to the mills. They would have to have an outlet for the resulting product, on which they would obtain no profit at first; but any progressive planter would be only too pleased to secure a better crop especially in view of the new method of payment on sucrose, and for that purpose he would need more fertilisers. He believed there would very soon be a large market for all those things.

Mr. Watson said it seemed to him that apart from this matter of waste waters and by-products their biggest trouble in Natal was the disposal of practically half their output of molasses. Mr. Blewett had mentioned that in Java and certain other countries they put the molasses on the land as a fertiliser and in that way got rid of it. There was no doubt the addition of this quantity of molasses to the waste waters was the cause of half the trouble in regard to sedimentation.

The Chairman said that from the results obtained in Mauritius, molasses supplied to the field would give very valuable returns. The only doubt was whether planters would like to try it and what one could do to induce them to take the molasses. If molasses was not used as a fertiliser or burnt, but was thrown out into the nearest river, that was about the most harmful thing that could be done with it. He had been many years on the North Coast and could say for a fact that he had seen dead fish in the lagoon at the Umhloti valley mouth, only on one occasion, when large quantities of molasses were dumped into the river. If molasses could not be used as fertiliser or sold for the manufacture of alcohol, there was no doubt the only thing to do was to try and burn it, but not to throw it into the nearest river.

Mr. Dodds remarked that in view of the excellent papers they had had from Messrs. Dymond and Blewett in pointing out the numerous valuable uses to which molasses could be put, it did appear deplorable that so much should be wasted in this country and turned into streams, instead of yielding the maximum benefit the molasses did the maximum amount of harm. It was a matter which obviously the industry ought to take up at the earliest possible moment.

He would like to endorse very fully Mr. Blewett's remarks regarding over optimism towards the fertiliser values of the product recovered by any treatment of waste waters. He thought in the early days of sewage treatment a great many promising schemes were damned at their birth owing to unfulfilled expectations regarding the valuable products anticipated in the form of fertiliser. It should be realised that any method of dealing with waste water was a charge on the main manufacturing process in getting rid of a harmful by-product, and should not be regarded as a source of profit as a fertiliser or the like, but if the product could be made to have any compensating value so much the better. Certainly all their soils did need organic matter very much indeed, especially soils which had been under cultivation of cane for some years; and it had been pointed out repeatedly it was most unfortunate that it was not practicable to make a business of selling organic matter as such, but only commercial (mostly mineral) fertilisers, which were very urgently required in their way, but which were not a complete plant food. A lot of work required to be done regarding the best means of supplying organic matter to the plant and also in demonstrating the value or necessity of it, experimental work which had only recently been begun, but which they hoped would lead to valuable results in the future.

Mr. de Froberville said regarding the point that had been raised about the mill residues: Ashes recovered from the furnaces are thrown outside on the bank of the river, if there is one close by, and are lost. Press cake is generally discharged into a place in the mill yard, where it undergoes spontaneous combustion and goes to waste. Molasses, when not taken by the distillery nor spread on the bagasse on its way to the furnaces, is generally discharged into the river. All these valuable residues are therefore, lost. Why should not a mixture of these three be made as is done in Mauritius, for the preparation of a manure or a fertiliser ? The heap is constructed thus: First a layer of press cake, then one of ashes and another layer of press cake and so on alternately until a reasonable height of some 9 or 10 feet of the mixture is obtained. Molasses is spread over the whole so as to keep the heap always saturated.

Keeping this heap constantly damp, fermentation sets in, the press cakes are disintegrated and the ashes get incorporated with the press cake and molasses, and after a few months, a mixture is obtained, which is richer than stable or farm yard manure and contains valuable plant food.

He had seen this practice carried on in Mauritius for years and the results obtained from the application of this mixture to the cane had been very satisfactory.

If then there is no means of getting rid of the surplus of molasses except by throwing it into the river, let some of it be burnt in the furnaces and utilize some also in the preparation of this compost until the time comes when each mill will have a distillery of its own. If some attention was given to this process of preparing a valuable manure, it would help in avoiding the danger of polluting rivers and streams.

It was distressing to see heaps of press cake in the mill yard, taking fire and emitting abominable smells. These residues lay there for years and are wasted, whereas in converting them into manure it would be taken by the planters for their own benefit.

Mr. Blacklock said he had a few notes, which were really an appendix to Mr. Blewett's valuable contribution on the utilisation of molasses. He had been deputed by the convenor of the Utilisation of Waste Products Committee to deal with the question of the manufacture of decolorising carbon.

Molasses Carbons

By L. Blacklock.

I have been deputed by the Convenor of the Utilisation of Waste Products Committee to deal with the manufacture of decolorising carbons from molasses. In the short time at my disposal I have found great difficulty in gathering any specific information regarding the production of this material. The notes made will serve to show that only very general outlines of procedure are available. Details being in the nature of trade secrets—and probably the result of lengthy investigation—are not divulged.

The actual carbonising of molasses is of course not a difficult matter, but the activation of the resulting carbon is not so easy.

In one method of manufacture an effort is made to have the carbon deposited in the cellular structure of porous inorganic material such as kieselguhr or pumice stone. Sometimes a liquid binding medium is used to facilitate this. Endeavours have been made to produce a nitrogenous carbon similar to that of animal charcoal by including in the general mixture before carbonising, matter such as gelatine, casein and albumen.

Modification of the above process consists of the carbonising of molasses mixed with an inorganic base which is afterwards separated from the deposited carbon by chemical means. Lime, chalk, calcium chloride or zinc chloride are bases named in this connection. The inorganic matter is subsequently leached or dissolved out by acid and the carbon separated by filtration. The object here is to produce a finely divided active carbon in a practically pure state instead of a carbon distributed through a porous structure. The presence of the inorganic material during carbonisation of the mixture, seems to prevent the formation of the hydro-carbon film covering the active carbon. This troublesome deposit occurs when vegetable materials are carbonised alone. Possibly the gases evolved by the decomposition of the inorganic substances during distillation or burning, assist in the formation of active carbon. Another modification given is the coking of the raw material such as molasses, and the extraction of the residue with a substance such as selenium oxychloride to dissolve the coking products. Carbons of this type are very active absorbants, but are obtained in an extremely fine state of division. The material "carboraffin" is mentioned as a type of this.

"Filtchar," "Suchar," and "Sulphite Carbon" are derived from sulphite liquor, a waste product of the paper mills.

"Norit," probably the best known active decolorising carbon is produced by the carbonisation of materials of vegetable origin and the subsequent activation of the resulting carbon by gases such as superheated steam or carbon dioxide at a temperature of 800 to 1,200°C. Possibly molasses could be used as a source of this carbon, but there are no records of its having been employed in this connection.

In 1922 Moriz Weinrich claimed to have successfully utilised waste molasses in the production of decolorising carbons more active than Bone Char. Weinrich was recognised for many years prior to his death in 1922 as one of the leading American experts on the use and treatment of Bone Charcoal. He directed his researches for a number of years along the lines of the utilisation of materials which would be otherwise classed as wastes. As a result of these investigations he claims to have produced effective decolorising and filtering materials that could be profitably manufactured at a relatively low cost. The main object of this process seems to be the production of a material consisting of a hard, mineral, porous framework covered by finely divided vegetable carbon —a material which may be used and revivified like Boneblack, but the cost of which would be much smaller than that of Bonechar. In this way he succeeded in making four kinds of filtering media as follows:—

1. A granular char as hard as boneblack made from molasses, lime, clay, etc., and to be used in cisterns like boneblack.
2. A fine granular char with some dust, for use in filter presses—made from molasses, lime and powdered carbonate of lime to be used on neutral or alkaline solutions.
3. A fine granular char with some dust—to be used in filter presses—made from molasses, lime and clay, etc. This lime to be leached out after burning by means of water and hydrochloric acid. This material is adapted to use on plantations where white sugar is being made from acid juices as for instance in Louisiana.
4. A pure or nearly pure carbon for use in filter presses made from molasses and lime mixture —the lime to be removed by dissolving out with dilute hydrochloric acid.

Experiments made with these materials at the Louisiana Experiment Station, in refineries, and on plantations were alleged to confirm the inventor's own tests showing a decolorising action greater than bonechar.

The proportions of materials to be used for No. 1 char are about as follows:—

100 parts by weight of blackstrap or molasses.
60 parts by weight of limestone..
150 parts by weight of clay.

Altogether 310 parts which would yield 220 parts of char.

An enormous volume of gas is given off during calcination by the molasses. The condensable portion of these will cover about half the working expenses. The uncondensable portion can be used as fuel.

Approximate cost of production of No. 1 char:—

100 tons molasses at 15/- per ton	£75
60 tons limestone at 15/- per ton	£45
150 tons clay at 25/- per ton	£187
Working expenses, say	£150
	£457
Value of bye-products, say	£60
	£397

100 tons molasses will give 20/25 tons of carbon and there would be left 220 tons of finished material costing 36/- per ton.

In the case of No. 2 char the cost of production may be roughly estimated as follows:—

100 tons of molasses at 15/- per ton	£75
100 tons limestone (half to be burnt to lime and the other half powdered unburnt)	£75
Working expenses as before	£150
	£300
Value of bye-products	£60
	£240

Amount of finished material—120 tons at £2 per ton.

No. 3 char called "Acid Proof Char" costs somewhat more:—

100 tons molasses, at 15/- per ton	£75
60 tons limestone at 15/- per ton	£45
100 tons clay, at 25/- per ton	£125
10 tons HCl, at 17/- per ton	£85
	£330
Less bye-products	£60
	£270
Workng expenses	£150
	£420

Yield 120 tons costing £3/10/- per ton.

South African cost of this material would be very much higher as HCl here would cost in the region of £40 per ton and approximately double the cost of the char per ton.

No. 4 char—Carbon:—

100 tons molasses, at 15/- per ton	£75
100 tons limestone burnt to lime at 15/- per ton	£75
12 tons HCl, say at £40 per ton	£480
Working expenses	£150
	£780
Bye-products	£60
	£720

Product 25 tons carbon costing in South Africa £28 per ton; the above would seem to indicate that something might be done in the matter of carbon production, but on the face of it, this branch of manufacture does not seem too promising as a means of disposal of molasses in quantity.

The paucity of information on this subject suggests another possible field for research which may be undertaken at some future time by the, I am afraid, already overworked Experiment Station.

Mr. Dodds pointed out that the tendency in this country for the last year or two, at all events, appeared to be to make somewhat lower grades of sugar and send them to a refinery to be converted into sugar for direct consumption. That was contrary to the tendency in most countries where it was usually an increasing practice to convert the product into sugar for direct consumption at the factory. To supply the requirements of that course a large number of vegetable carbons had been devised and placed on the market during the last few years, none of which apparently were quite perfect for the purpose up to the present. What was really required was a vegetable carbon which could be produced sufficiently cheaply to be discarded after it had been used in the factory, instead of being subjected to an expensive and troublesome treatment of revivication, which was a necessity in the case of most carbons. Another requirement that applied to an isolated country such as this, at all events, was a carbon that could be manufactured locally and not imported. Even the few carbons which were made in other countries and sold cheaply enough to be discarded, would not be nearly cheap enough for that method after exportation over here. Several possible local sources of a suitable carbon occurred to one. Apparently almost any waste organic material could be converted into decolorising carbon by suitable treatment. They had in this country molasses, which as Mr. Blacklock had pointed out might be used, also bagasse, and it had occurred to him (the speaker) that possibly the waste bark or wood fibre from wattle extract manufacture might be a suitable source. At all events, it appeared advisable to carry out experiments to determine whether any of these sources could furnish a suitable kind of carbon for their conditions.

There being no further question or comments, the Chairman called upon Mr. Rault to read his paper on "CLARIFICATION & FILTRATION."