Wastes- Solids, Liquids and Gases

A SYMPOSIUM PRESENTED
AT THE LAST TWO ACHEMA
MEETINGS: 1967, 1970
FRANKFURT/MAIN, GERMANY

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Preface

For the last half century, at three-year intervals, the European Federation of Chemical Engineers has presented international exhibits displaying the latest state of the art, at Frankfurt, Germany. These recurrent events are generally coincident with lectures and discussions by technical experts.

Also, special committees have been formed on subjects of particular significance; thus since 1964 there has been a group dedicated to the preservation and protection of the environment.

The 1967 convention produced, among others, some new insights into the field of suspensions and aerosols. Five of the twenty-four lectures were presented in English.

At the 1970 convention, the opening paper was read by a noted American authority on the aspects of water supplies and their maintenance, in English. Two other contributions were likewise in English.

The bulk of the material, mostly case histories, was presented in the German language. In view of its wide interest, a translation is submitted herewith. The permission granted by Dr. D. Behrens, Managing Director of Dechema, is gratefully acknowledged.

June, 1972
Tampa, Florida

Max F. Wulfinghoff

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Clean Water in the Chemical Industries

W. Teske, Ph.D., Hoechst, Germany

In view of recent legislation, some significant figures will be quoted for West German conditions, as of 1966. Main users were:

	billion cu. meters
The chemical industries	2.756
Coal mining	2.733
Iron and steel	1.267
Paper and pulp	0.816
Oil refining	0.432
Minerals	0.302
Automotive and aircraft	0.239
Textiles	0.254

The total water supply in West Germany in 1963 was 13.34 billion cubic meters, of which households took 2.61 billion and industry 10.73 billion or 80 pct. Of the latter, chemical industry took 25.6 pct of which 80 to 85 pct was cooling water, and balance production use. The waste water produced by all industry amounted to 9.78 billion cubic meters, of which 2.65 billion or 27 pct was due to the chemical industries. Of this, 2.09 billion was cooling and hence unpolluted water or 79 pct. 0.462 billion cubic meters or 17.4 pct, were loaded with chemicals, and discharged into rivers or sewer systems. Again, 0.362 billion of these were treated to some extent (11.5 pct) and 0.157 billion remained untreated (5.9 pct).

In order to prevent any lasting damage to the physical, chemical or biological characteristics of waters, extensive legislation has intervened since 1965. The principles and technology of

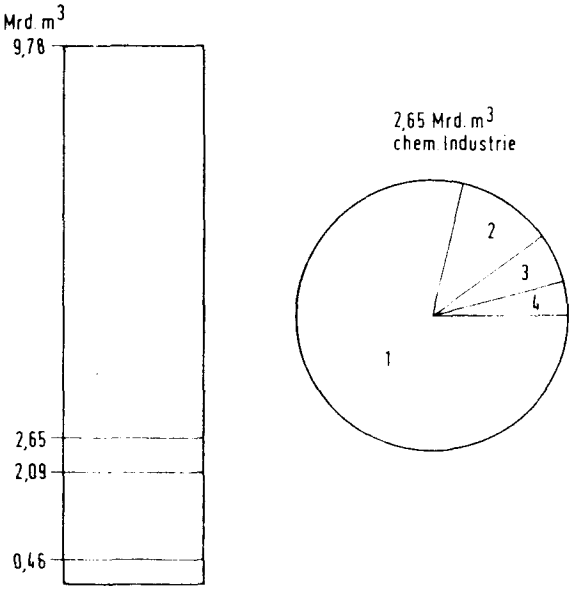

Fig. 1 At left, total of industrial waste waters, 9.78 x 10^9 m^3, of which 2.65 x 10^9 is due to chemical industries comprising 2.09 x 10^9 m^3 cooling water and 0.46 x 10^9 m^3 of polluted material. At right, individual components by percentages: 1 = coolant (78.8), 2 = partially treated (11.5), 3 = non-pretreated (5.9), balance unused waters (3.8).

such treatment have been discussed in a prior publication, as settling, separation, filters, steam and air stripping, biological percolation, accelerators and sludge tanks. Also, aeration ponds are in use; Fig. 2 shows an installation situated at Geleen, Holland, and belonging to the Staatsmijnen operation. In principle, such plant-owned clarification equipment could be circumvented through direct introduction of waste waters into natural or artificial subterranean cavities, provided that ground water supplies are not interfered with.

In Germany, such opportunities are rare, as abandoned salt mines may not be utilized in view of possible damage. In Midland, Michigan, the Dow Chemical Co. is said to dispose of one-third of its effluents demanding 60 tons per day of chemical oxygen by means of subterranean deposition.

By another method, waste waters that are impractical to recondition are disposed at sea. This is practiced by some German firms in the case of iron-bearing sulfuric effluents from titanium

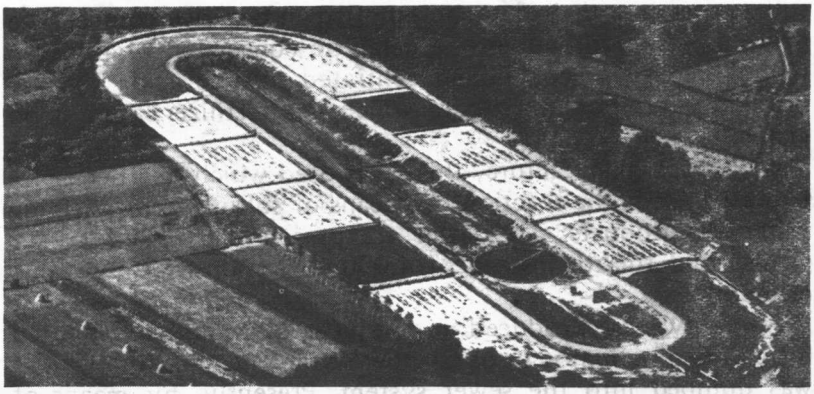

Fig. 2 Oxidation ponds

white production, of gypsum-bearing sludges, of concentrated salt solutions, and of toxic wastes the biological treatment of which would be overexpensive. The matter is under study by a special committee. Whether chemical companies should provide water treatment facilities of their own, or join forces with a publicly owned installation will depend on circumstances such as the need to provide canals, holdover ponds, pretreatment plants or the like. On the other hand, the privately owned plant will be less dependent on overall changes in the local industry, or variations in water purity and composition, etc. In any event, changes or improvements in the manufacturing process itself offer possibilities. Thus, for a large petrochemical plant the BOD_5 content of the waste waters was reduced by 6 tons per day through a stripping process. Vast amounts of hydrochloric acid had become unsaleable; they resulted from the chlorination of hydrocarbons. In 1965 an electrolytic department was added that produces 100 tons per day of commercial chlorine from these effluents.

Other operations leave bisulfite-bearing effluents that consume oxygen and are presently reworked to yield commercial sulfur dioxide. Surplus phenol is recovered in another department. Ethylene oxide production by the chlorhydrine process had supplied some 100,000 to 250,000 tons of calcium chloride solution that now undergo direct oxidation.

In the production of perlon, caprolactam had been made through a conversion of sodium nitrite, sodium sulfite and sulfur dioxide in an aqueous solution, and 3000 tons of sodium

sulfate per month had to be emptied into a rivercourse. The process was modified into a catalytic conversion of nitrogen monoxide, hydrogen and concentrated sulfuric acid. The by-product is ammonium sulfate which is a fertilizer; there is no effluent.

In rubber manufacture, thiazol is used which had been precipitated from the reaction by means of sulfuric acid, yielding watery byproducts. The latter are presently oxidized by air, giving solid thiazol instead of 4,000 tons monthly of organic effluent.

Some dyes are produced in a water solution and precipitated by means of common or of Glauber's salt. The aqueous effluent was dumped into the sewer system. Presently, by means of spray drying the dyes obtained are in powder form, and no waste water is produced.

The reduction of organic compounds was commonly achieved by means of iron, and the remaining ferrous sludges and salts created a problem. Meantime, the iron could be replaced by hydrazin hydrate that leaves no residues, or by pressurized hydrogen.

Finally, water cooling systems have largely been replaced by recirculation via towers, or by air cooling, all of which has reduced the load on water disposal systems.

Centralization of Waste Treatment Installations

In areas where chemical industries are concentrated, a variety of effluents may become available, and the question arises as to the advisability of a common treatment facility. Questions that will have to be asked comprise:

1. Can the effluent be decomposed by biological means?
2. What is the biological and the chemical oxygen demand?
3. How much sludge can be expected to accumulate in the treating chamber?
4. What is the sludge/recycle ratio?
5. Quantity of excess sludge?
6. Overall oxygen demand?
7. Oxygen resorption; demand of air?
8. Nutrient requirements?
9. Expected degree of decomposition?
10. Shape of pond if available?
11. Rate of recirculation?

12. Energy requirements?
13. Times of aeration? (Holdover time)
14. Pre-clarification time?
15. Post-clarification time?

In this connection, a direct extrapolation of laboratory results would be inadvisable in view of the considerable first cost and operating expense of such a facility; use of a pilot or semi-works plant is recommended; note Fig. 3.

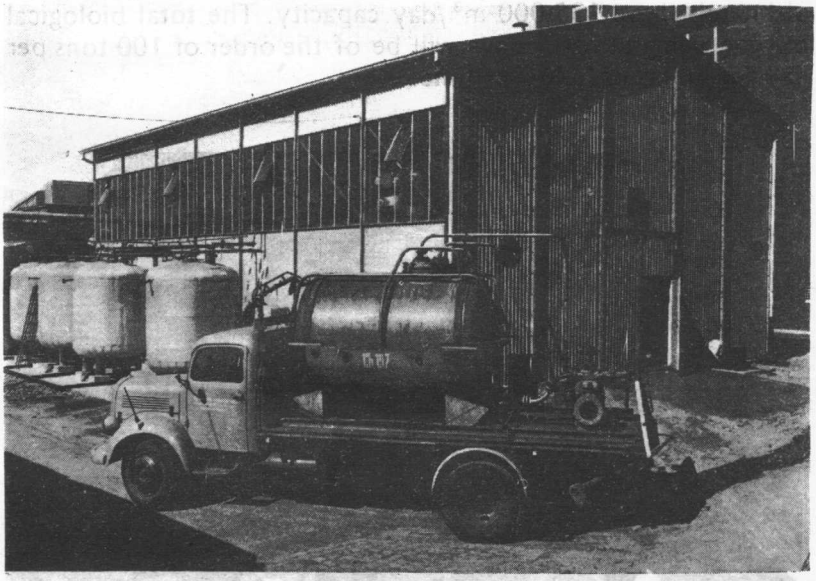

Fig. 3 Mobile test equipment, Hoechst AG

In the typical case, the planning requires a large number of individual answers from chemists, biologists, process engineers and constructors, aided by electronic data processing. In most cases, better separation of cooling water streams from contaminated waters will be indicated. The environmental relationships merit particular attention, especially so since water treatment plants are unproductive users of space. For instance, some concerns that have such facilities under construction include E. Merck of Darmstadt, Boehringer of Ingelheim, Erdoelchemie of Dormagen, Huels, Schering, Hoechst, Bayer of Leverkusen, BASF of Ludwigshafen, and others. Bayer and BASF have

joined forces with a neighboring community; Fig. 4 is a scale model. Here, two rivers and several highways had to be rerouted. 1a is the community's pretreatment plant featuring a mechanical filter, sand filter, and presettler. 1b is the industrial pretreatment and biological stage. At 4 a holdover tank for acid effluents is provided, including a neutralizer. At 2 solid and sludges are deposed, and at 3 an incinerator is planned. The capacity is 65000 cubic meters daily; the first stage opened in 1968 handles 34,000 cubic meters per day. Furthermore, the facility will deal with the effluents of five corporations, and ultimately have 135,000 m^3/day capacity. The total biological oxygen demand for 5 days will be of the order of 100 tons per day for 36 hours holdover time.

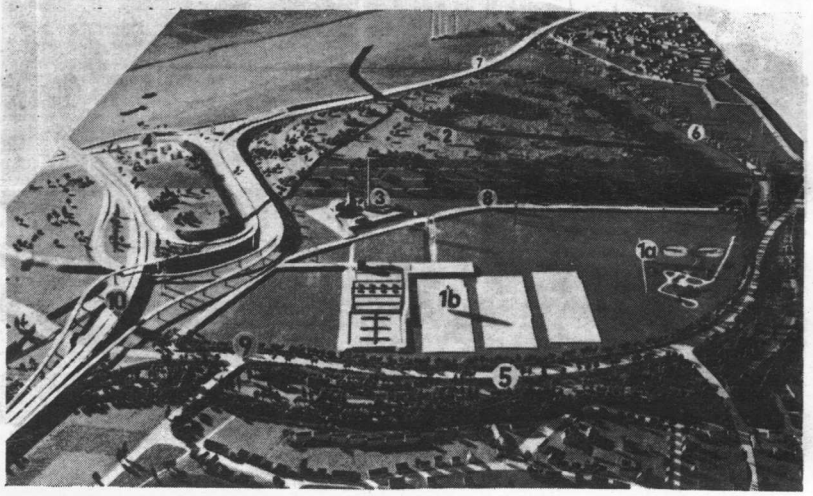

Fig. 4 Scale model of Bayer plant

Likewise, BASF expects to treat its plant effluents together with the city wastes of Ludwigshafen. The industry will supply 250,000 to 300,000 cubic meters daily with an oxygen load of 170 to 200 tons per day. Here, the plant effluent carries nitrates and nitrites that cannot be degraded adequately by biological means in the usual manner. A two-stage decomposition is required that consists of one denitrification tank where the bacteria remove their oxygen demand by degrading the nitrates and nitrites, and one standard aeration tank. The excess sludge will

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be composted after mechanical dehydration. To collect the effluents, a second waterway of 25 km total length must be provided.

Fig. 5 is a view of the Huels facility. Per day 72,000 cubic meters of plant effluent must be treated biologically. After a mechanical pretreatment, the waste water is forwarded to the large pond. First it is sprayed to remove the volatiles and pick up the oxygen needed for the following biological stage. Further aeration takes place in the pond itself.

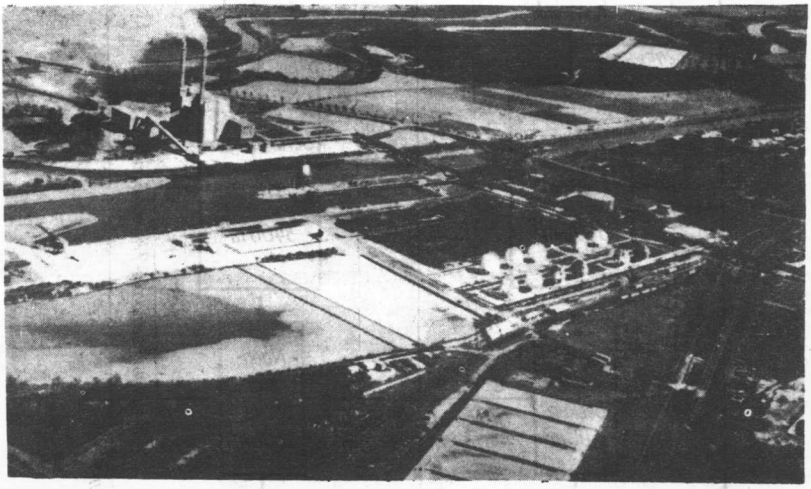

Fig. 5 Plant of Chemische Werke Huelst

The installation of Merck is a closed one as it includes the mechanical and biological purification, and incineration of the excess sludge. It handles 24,000 cubic meters of effluent daily with a biological oxygen demand of 28 tons. The waste waters first pass a sand trap and screen and a neutralizing station followed by an aerated sand zone, and flocculating and settling space. The remaining sludge is deposited on drying beds. The waste then enters three holding and storage tanks of a total of 42,000 m^3 where it is homogenized by repeated recycling. Like in the Huels case, it is made to form an air curtain. The treatment is by three accelerators of the aerating type, each 30.5 m in diameter and 6.6 m deep, followed by a thickener and sludge storage.

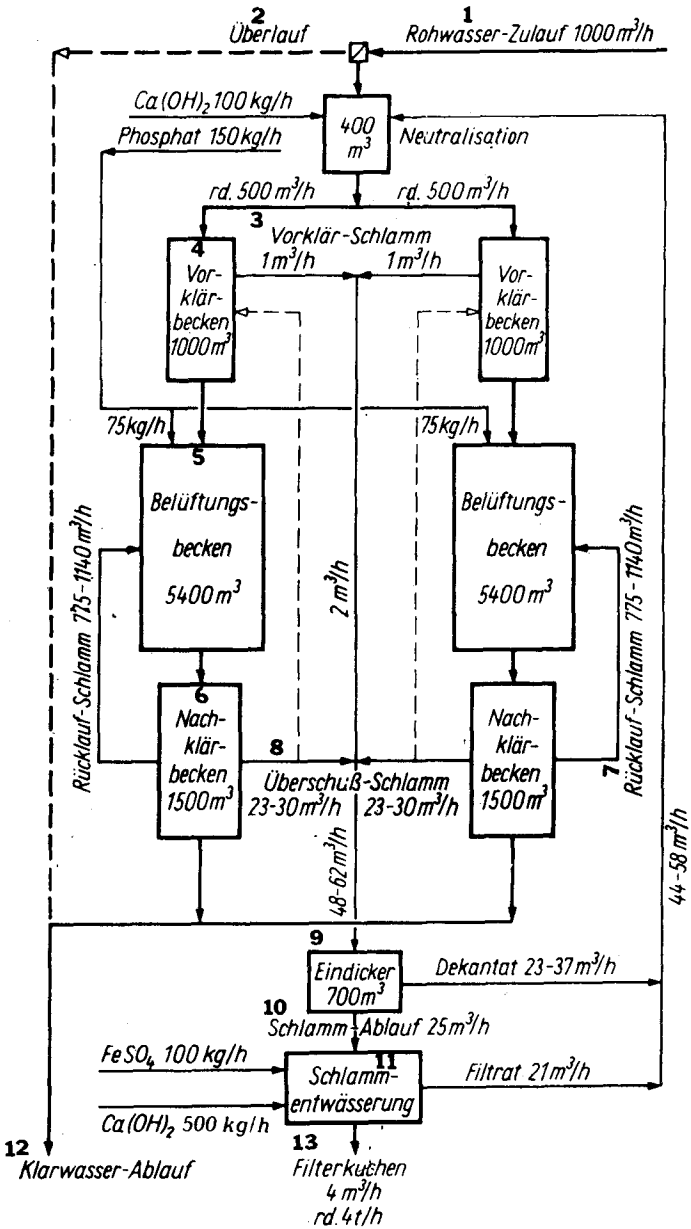

Fig. 6 Flowsheet of Hoechst plant—1. Raw water in, 2. Overflow, 3. Pretreated sludge, 4. Pretreating tank, 5. Aeration tank, 6. Postclarification tank, 7. Recycled sludge, 8. Excess sludge, 9. Thickener, 10. Sludge exit, 11. Sludge dewatering, 12. Clear water runoff, 13. Filter cake.

The biological treatment takes 4 hrs. and is 95 percent effective. The excess sludge is filtered after pre-thickening and addition of ashes, iron sulfate and lime to give a firm product which passes to the incinerator. The kiln is oil fired and has five stages through which the sludge passes downward and is eventually ignited at 800°C. and incinerated.

At Hoechst, 100,000 m^3 of effluent per day are treated in four stages, with a biological oxygen demand of 120 tons. Fig. 6 presents the first stage for 24,000 m^3/day. The effluents are loaded with organic petrochemicals and are first neutralized with lime. The resulting solids are separated in two tanks, and forwarded to two activated sludge ponds, after pre-clarification. Aeration is by 16 Vortair surface ventilators, the residence time is 10.5 hours. Post-clarification takes place in two ponds. Filtration is by two filters; lime and iron sulfate are added and the sludge is deposed temporarily, Fig. 7. Later it will be incinerated. Space limitations require operation at a relatively high oxygen demand level of 1200 mg-per liter. The decomposition is 95 pct complete. The phosphorus and nitrogen demand of the bacteria could not be supplied from domestic sewage, so fertilizer out of the current production must be added.

To sum up, since all antipollution work is expensive, it must ultimately be paid out of current revenue. Therefore the ques-

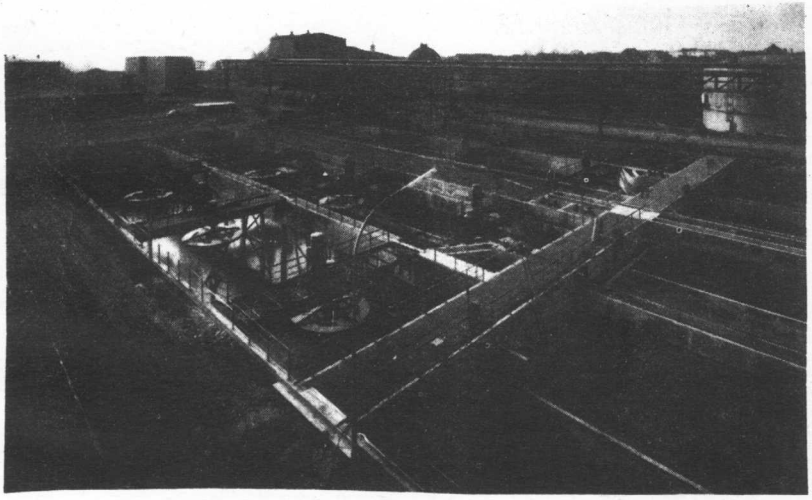

Fig. 7 Biological treatment at Hoechst

tion cannot be what is feasible, exhausting all possibilities; rather, one has to consider how much one can afford to buy in the way of antipollution equipment in view of the need to maintain one's ability to compete in the domestic and possibly the world markets.

On the Shear Strength of Flocs

Friedrich Benze, D. Ing., Aachen, Germany

In recently developed water purification schemes, a separation of solids from liquids by means of centrifugals is encountered frequently. In that connection the effect of the transverse motion upon the flake size, the mechanical strength of the floc and the floc volume are of special interest.

The coagulation of particles in suspension is controlled by the interaction of repulsion and attraction potentials. The attraction of particles is due to Van der Waal's attractions that are far-reaching cohesive forces. The repulse potential is due to the boundary layer potential in the electrical double layer at the solid-liquid interface, and it may be found from electrophoresis tests.

When coagulating the particles must overcome the potential threshold. The energy of interaction that slows down or impedes coagulation can be reduced by adding an electrolyte that lowers the boundary face potential. Another way is offered by an increase of the kinetic energy of particles by drawing energy from the viscous flow or by temperature increase. Along with such energetic considerations the geometry of flocculation must be considered. The Brownian molecular motion offers the particles an opportunity to contact each other and thus coagulate. Stirring the suspension will improve the resulting probability.

Smoluchowsky was the first to calculate the probability of impact due to the Brownian motion as well as velocity in a laminar shear field; note tabulation in Fig. 1

The speed of coagulation due to Brownian motion depends only upon the temperature and the viscosity. The coagulation

Probabilities of impact (from Smoluchowski).

Brownian molecular motion $$b_B = \frac{8}{3}\frac{kT}{\eta} n_1 n_2$$

Motion under shear $$b_G = \frac{4}{3} G (r_1 + r_2)^3 n_1 n_2$$

$$= \frac{4}{3} G R^3 n_1 n_2$$

Ratio of probabilities of impact:

$$J = \frac{b_G}{b_B} = \frac{\eta R^3 G}{2 k T}$$

Diameter of particle (μm)	$J = \frac{b_G}{b_B}$		
	$G = 1\ sec^{-1}$	$G = 10\ sec^{-1}$	$G = 100\ sec^{-1}$
0.1	10^{-4}	10^{-3}	10^{-2}
1	10^{-1}	1	10^{1}
10	10^{2}	10^{3}	10^{4}

($\eta = 1 \cdot 10^{-2}$ Poise, $k = 1{,}38 \cdot 10^{-16}$ erg/Grad, T = 300°K)

Fig. 1

due to the velocity gradient is proportional to the shear gradient G and the particle size. The probability of collision for the particles and hence the decrease in time of the free suspended particles is an additive resultant of the chance of collision due to Brownian motion and the laminar shear.

It can be shown that for small particles the chance of collision is mostly due to Brownian motion and agitation has no effect on flocculation. For large particles the effect is the reverse. The ratio of these probabilities:

$$J = \frac{b_G}{b_B} = \frac{\eta G R^3}{2 k T}$$

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