

MEASURES AGAINST WATER POLLUTION IN INDUSTRIES PRODUCING BASIC INORGANIC CHEMICALS INCLUDING FERTILIZERS

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ABSTRACT

The chemical industry began at an early stage to take pains to make further use of unwanted by-products from chemical reactions. When these products became a nuisance to the environment, further processing became a necessity. Economic interest was also involved in many cases. Thus the barium chloride solution obtained in the production of lithopone is converted into BaSO_4 or BaCl_2 . By the Claus process sulphur is reconverted from CaS , the waste product of the Le Blanc soda process.

However, many processes have waste products which can only be put to further use with difficulty. Increasing industrialization and population density limit the possibility of dumping these substances in rivers. The method of biological processing which has proved successful for organic waste is restricted to exceptional cases. Most of the remaining processes are costly. Waste sulphuric acid from the production of pigments and dyes is either boiled down and the salt thus achieved converted into SO_2 , or it is transported out to sea where it is pumped out to be diluted with sea water to a high degree. The residue from the production of hydrogen fluoride from fluospar is converted into anhydrite and sold to the building industry. In many cases the problem of waste products can be solved by changing the method of production. One example of this is the production of TiO_2 by the titanium tetrachloride process instead of by the sulphuric acid process. The best position for production processes where unavoidably large quantities of waste salt are produced is on the coast. The possibility of the sea as a dumping ground will become increasingly important for the industry in the future.

EFFLUENT PROBLEMS IN THE CHEMICAL INDUSTRY

In chemical processes new substances are obtained from existing ones through reactions between materials in the gaseous, liquid, or solid state. But as the end products of chemical reactions are not always saleable, those of them which represent undesirable by-products have either to be discarded or fed back into the production process after suitable treatment. Where the latter has been commercially rewarding it has always been the more attractive course. In addition attention has been paid for many years to the problems of disposal and

recovery in cases where by-products constitute a serious threat to the environment. Frequently, however, by-products are substances which can be discharged into receiving waters without risk to humans, flora, or fauna. As industrialization and population densities increase, the opportunities for disposal in this way are bound to become more limited. That is the stage in which most industrialized countries find themselves today. Organic waste substances can be degraded biologically. But such methods are only suitable in exceptional cases when applied to inorganic substances. Where they are concerned other measures are needed. Among the most important of these are changes in production processes.

With reference to a fairly large number of examples an attempt will be made in what follows to illustrate the problems raised by effluents from inorganic production. Owing to lack of space only the most important processes will be mentioned.

PURIFICATION OF EFFLUENTS AND REMOVAL OF RESIDUES

Dissolved gases

In the production of inorganic acids small amounts of starting products, which are usually gaseous, get into the water. In sulphuric acid production the SO_2 which has been washed out of the waste gases is recovered by blowing gases through the washing solution and it is then recycled. Previously oxidized SO_2 is, however, lost in the form of waste acid. In nitric acid production a small proportion of the nitrous gas produced (up to 1 per cent) is discharged into the receiving water in the form of highly dilute nitric acid. The gaseous hydrogen chloride which is formed in the various chlorination processes, particularly when these are used to treat organic substances, can be recovered by the hydrochloric acid electrolysis process. In the production of ammonia up to 0.1 per cent of the NH_3 obtained is lost in the form of a dilute solution. Other gaseous substances which may occur in aqueous solution include hydrogen sulphide, which may be formed in the production of such sulphidic pigments as lithopone and cadmium sulphide, and hydrocyanic acid, which may be present in waste water from galvanic baths. Owing to their toxicity both of these must be oxidized, particularly when the drain waters are acidic. Generally they are oxidized with chlorine.

Liquids

Turning to liquids, we find that the most important are waste acids. Waste acid is formed in the production of titanium dioxide pigments when the titanium sulphate solution is hydrolyzed.

Further amounts are obtained in the production of sulphuric acid. When the burner gases are being washed out, the water absorbs so much SO_3 that a 35 per cent sulphuric acid is obtained. Though long used in the fertilizer industry, this has recently become more difficult to sell owing to its content of iron sulphate and other substances.

Waste sulphuric acid is now being dealt with in two ways. The first is to increase the concentration of the acid with submerged flame burners to 60–70 per cent, which entails the filtering off of a mixture of sulphates of the alkali

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metals, alkaline-earth metals, earth metals, and iron. Then the acid can be concentrated to 95 per cent in steel vessels and used again, *e.g.* to dissolve the ilmenite. The filter salt is split up by being exposed to a temperature of 400°C in the presence of lignite or sulphur. The SO_2 thus formed is used in the production of SO_3 . The residual substances are oxides, which can be dumped on a tip without harm to the environment.

The second way of dealing with waste sulphuric acid is as follows: the acid is filled into rubber-lined tanks through plastics pipes and then taken by ship to the sea; there the acid is released behind the screws of the ships, which causes it to be diluted in a ratio of about 1 : 7000 and thus neutralized. If the diluting media were pure water and not sea water, this process of dilution would cause a reduction of the concentration of SO_4 ions to about 30 mg/litre and of Fe ions to about 5 mg/litre. Owing to the high degree of dilution the amounts of heavy metal ions present in the waste acid do not raise the concentrations present in the sea.

For the treatment of hydrochloric acid, the oxidation processes with nitrose (Kellog), with oxygen of the air and catalyst (Deacon), with oxygen of the air via intermediates, and as the most important one, the electrolysis have been developed. Here gaseous hydrogen chloride is used for raising the concentration of the electrolyzed hydrochloric acid. This process does not result unavoidably in the production of caustic soda solution and is therefore particularly suitable when industry needs only chlorine.

Solids

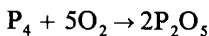
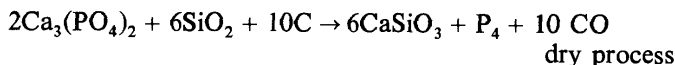
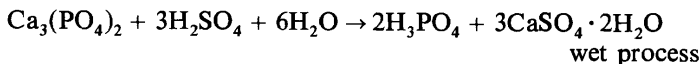
Very fine-particled solids that are difficult to remove from the water are obtained in the production of inorganic pigments and other solids, as in the manufacture of silica fillers by the aqueous process and in the manufacture of iron oxide pigments, titanium dioxide, cadmium sulphide, lithopone, vitreous enamels, and activated carbon. These residues have particles ranging in size from 10 microns to 0.01 micron. They are precipitated by sedimentation in large concentrators, usually with the aid of flocculants. In as far as they are not fed back into the process, they can be dumped on a tip without risk.

In the production of hydrofluoric acid, fluorspar is reacted with sulphuric acid at $200\text{--}300^{\circ}\text{C}$ in rotary kilns to give calcium sulphate and hydrogen fluoride. The hydrogen fluoride is used mainly for refrigerants and spraying agents, *e.g.* dichlorodifluoromethane, as well as for fluxes in the aluminium industry. In the past, the by-product, calcium sulphate, was discharged into receiving waters. But for a number of years it has been neutralized through addition of CaO and used in the production of anhydrite, which is a building material. If the anhydrite is to be satisfactory, the reactions have to be carried out under definite conditions and even the fluorspar has to be carefully chosen. For every ton of hydrofluoric acid there are 3.7 tons of CaSO_4 by-product, which has to be dealt with somehow or other. Another possibility would be to use the CaSO_4 for the gypsum sulphuric acid process, which is now still in use at only a few places in the world.

Large quantities of fluorine compounds are also obtained in the phosphate industry, where apatite is treated with sulphuric acid or nitric acid. The fluorine contained in the apatite goes into the gas phase, primarily in sulphuric acid

treatment, in the form of SiF_4 . The latter is washed out of the gases by means of water, but is not, at present, recovered to any greater extent. Suitable processes are being developed.

CaSO_4 is also a by-product of the manufacture of phosphoric acid by the wet process, in which calcium phosphate is reacted with sulphuric acid. Here it is obtained in the form of gypsum, which is now being dumped on tips.



Chemically purer phosphoric acid is usually produced by combustion of phosphorus, which is again obtained thermally by reacting calcium phosphate with SiO_2 and coal. A by-product of this reaction is calcium silicate, which, apart from being dumped on tips, is employed for useful purposes such as road and dam building. The waste gases formed in this process are washed. The washing water contains phosphorus and small amounts of hydrocyanic acid and therefore has to be oxidized with chlorine before being discharged into the receiving water.

A large amount of 'green salt' ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) is formed in the production of titanium dioxide pigments, the rate being 3.5 tons for every ton of TiO_2 . Usually titanium dioxide pigments are produced from ilmenite ($\text{FeO} \cdot \text{TiO}_2$). This material is dissolved in 96 per cent sulphuric acid. The solution is cooled until the majority of the simultaneously dissolved iron is precipitated as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (green salt), which is removed by filtration. Green salt can only be utilized to a limited extent. Some of it is used as a flocculant for biological sludges. Large amounts are dried and broken down chemically, the SO_2 thus liberated being used in sulphuric acid production. Some of the remaining iron oxide is used in the blast furnace process. As the processing of the iron sulphate represents an important cost factor, ilmenite is now treated metallurgically with coal and lime for the purpose of removing its iron content. The enriched titanium dioxide derived from this process is known as titanium slag. It is now a favoured raw material for titanium dioxide pigments, but the amounts available are not yet sufficient.

Dissolved substances

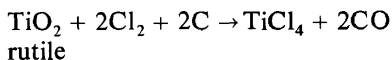
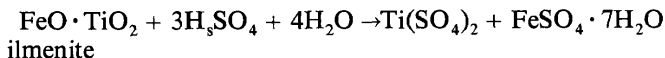
In terms of quantity the most important group is that comprising dissolved substances. In many chemical processes reactions between dissolved salts produce solid substances which are precipitated and filtered off. The undesired by-products remain in solution. In other processes solids are treated with chemicals and afterwards thoroughly washed. The washing liquids, which contain salts, are discharged into receiving waters.

Recently, owing to the growth of industry and large cities, the risk of excessive effluent concentrations in receiving waters has however increased, and it is still more likely to do so in future. The Rhine, for example, carries away about 30 000 tons of salt every day, almost half of which comes from the

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Alsatian potassium mines. At low water levels the salt concentration of the Rhine on Dutch territory reaches 300 mg of NaCl per litre. Upwards of 350 mg per litre the salt affects the taste of the water.

Among liquids, waste acids have already been mentioned. These have high salt contents. Spent acid from titanium dioxide production, for example, contains about 9 per cent of iron sulphate. Disposal of spent acid and 'green salt' therefore represents an important cost factor in the production of titanium dioxide pigments by the sulphuric acid process. Some titanium dioxide manufacturers have therefore transferred their plants to the coast in order to reduce the distance to the sea.



Another process for the production of titanium dioxide, which could substantially solve the disposal problems, has been gaining importance during roughly the last ten years. It is based on rutile, which is mixed with petroleum coke or other carbon-containing material and exposed to chlorine at a temperature of 1000°C. The titanium chloride formed is separated from other chlorides by distillation and reacted with oxygen at 1000°C. Titanium dioxide and chlorine are obtained; the latter is recycled. The process has proved so interesting to many producers that rutile is in short supply and for that reason the process is not economical at present. Attempts are being made to produce a high-percent titanium dioxide from natural TiO_2 -containing materials and thus to reduce the costs of the starting material.

In the production of silica from aqueous solution, water glass is reacted with dilute sulphuric acid. Apart from fine-particled silica, which is thickened and removed by filtration, sodium sulphate is formed at the rate of 0.7 ton per ton of SiO_2 . In the past this sodium sulphate has always been discharged into receiving waters. Its formation can be prevented by reacting the water glass with CO_2 instead of with sulphuric acid. Under suitable circumstances the sodium carbonate or sodium bicarbonate formed can be recovered. Water glass can be dispensed with by reacting SiO_2 with chlorine in the presence of coal, a process similar to that employed in titanium dioxide production. The result is silicon tetrachloride, which is then reacted with oxygen and hydrogen (oxy-hydrogen flame) to give SiO_2 and HCl . The products of this thermal process differ considerably in their properties from products obtained by the wet process.

Activated carbon is produced in two ways. Firstly it can be made by treating recent fuels, such as peat and cellulose, with dehydrating agents, *e.g.* zinc chloride, calcium chloride, sulphuric acid, and phosphoric acid, at 400–800°C. After this process of activation, the dehydrating agent must be removed by a washing operation. When ZnCl_2 is used, an acid zinc chloride solution is obtained; this is neutralized with zinc oxide, concentrated, and then recycled. In the washing-out process between 20–40 per cent of the zinc chloride gets wasted. As precipitation and recovery of the zinc in dilute solutions is very expensive, attempts are now being made to replace zinc chloride by an activating agent free from heavy metal. The second possibility of producing

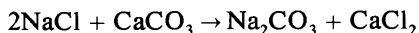
activated carbon is free from waste water problems. It consists in activating highly carbonized material with steam or CO_2 at 800–900°C.

To produce lithopone, barytes is used as the starting material and reduced with carbon in rotary kilns to barium sulphide. This is dissolved and reacted with a mixture of zinc chloride and zinc sulphate, depending on the desired ZnS content of the white pigment.



The ZnS alone, or ZnS and BaSO_4 , which are precipitated in the reaction, are calcined and aftertreated to develop their pigment properties. Barium chloride remains in solution. The process is more economical if, as has been done for many years, the barium chloride is concentrated and recovered or reacted with sodium sulphate to give barium sulphate, which, as blanc fixe, has many applications. Following the calcination, the lithopone is usually acidified to remove the undesired ZnO formed. The resulting zinc salt solution is discharged into receiving waters, which means that about one ton of zinc is lost per hundred tons of lithopone. Various processes have been developed for recovering the zinc. The production of lithopone no longer plays a substantial role today, because this pigment has lost much ground to titanium dioxide, with which it has to compete.

In the production of soda by the Solvay process, common salt in aqueous solution is reacted with ammonia and CO_2 under pressure. NaHCO_3 is precipitated and NH_4Cl remains in solution. Ammonia is driven out of the solution with calcium hydroxide, which results in the formation of calcium chloride. When heated, NaHCO_3 gives the soda required. The summary equation is:

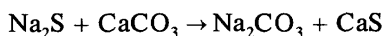


The by-product, calcium chloride, which cannot be utilized, is discharged into the receiving water following removal of the solid substances, such as calcium carbonate and calcium sulphate. Recently the United States government has been encouraging manufacturers to crystallize CaCl_2 by evaporation of water and thus to arrive at their sales product.

The salt burden on the receiving water can be avoided by starting from NaOH instead of NaCl and reacting the former under pressure with CO_2 (from flue gases), NaHCO_3 being formed. A further possibility consists in coupling soda production and alkali electrolysis. An NaCl solution is only partly electrolyzed by the diaphragm process, the chlorine formed is removed, whereafter CO_2 and subsequently NH_3 are passed into the solution, which contains the caustic soda solution in addition to sodium chloride. This causes precipitation of NaHCO_3 . The NH_4Cl formed is reacted, by adding further NaOH, to give NaCl and NH_3 . The ammonia is recycled into the process, the solution, whose NaCl content is now low, is raised to a higher content, by adding NaCl, and is again introduced into the diaphragm cells.

In the course of time the Solvay process has replaced the older Le Blanc soda production process. This was based on sodium sulphate, which was reduced and reacted with calcium carbonate.

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This process yields 1.5 tons of residues per ton of soda. They consist mainly of CaS, and their removal has caused considerable difficulties. When dumped on a tip they reacted with damp carbon dioxide to form H_2S . Sinking them in the sea was not an ideal solution either. Later the CaS was treated with carbon dioxide and moisture to drive out hydrogen sulphide, from which sulphur was recovered in a Claus furnace.

In Europe the treatment of phosphates with sulphuric acid is now less important than their treatment with nitric acid. The raw phosphate is first dissolved with nitric acid, and the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ formed is separated wholly or partly by cooling the solution down and filtered off. The mother liquor is neutralized with ammonia and boiled down. The calcium nitrate is used for producing calcium ammonium nitrate by admixing ammonium nitrate. The fertilizer industry's effluent problems arise from washing of the waste gases. In the treatment of phosphates, fluorine, for example, is liberated in the form of silicofluoride. In the past silicofluoride has been discharged into receiving waters with the washing water. But recovery of hydrogen fluoride from this compound is likely to become commercially interesting. In all fertilizer processes small amounts of fertilizers get into the waste gas in the form of dust during the formulating and drying operations; they are then dissolved in or precipitated by the washing water, with which, therefore, they are discharged into the receiving water. Here a closed cycle for the washing process, followed by evaporation, could possibly be introduced if the concentration of effluents in the receiving water threatens to become excessive.

PROBLEMS AND MEASURES OF THE FUTURE

Because of the growth of industry and population the amounts of waste substances needing to be disposed of are continuously increasing. Because of the importance of rivers as drinking water reservoirs increasingly strict requirements will have to be laid down with regard to the treatment of effluents that are discharged into the rivers. The usual biological methods used to degrade organic waste substances are only effective in exceptional cases where inorganic compounds are concerned; other techniques will therefore have to be found. Making a saleable product from the waste is one of the possibilities, provided there is an appropriate market for such a product. In very many cases changes of the process will have to be considered with a view to arriving at different by-products. The question of site is of particular importance. Location on a small receiving water is unfavourable. That is one of the reasons why, a hundred years ago, the German chemical industry sited its factories in the vicinity of large receiving waters. In future sites not far from the sea will be under heavy demand. The purification of inorganically loaded waste waters can then be confined to retaining solid substances, and to processing or converting into other products those dissolved substances that might disturb or harm marine organisms. If effluents could be discharged at places where the sea is very deep, that would be ideal. Consultation on an international level between industry, science, and conservation authorities with regard to the opportunities offered by the sea as a receiver of effluents is desirable.