

# THE CONTROL OF WATER POLLUTION AND THE DISPOSAL OF SOLID WASTES IN THE INDUSTRIES PRODUCING BASIC INORGANIC CHEMICALS

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**Abstract**—An outstanding change since the last Congress in 1970 has been the greatly increased sophistication of the approach to environmental problems. It is no longer adequate to consider only the direct immediate local effects of manufacturing activity, but it is also necessary to take into account environmental effects, possibly extended widely in space and time, arising both from effluent streams and man's use of the products of these activities. The shortage of raw materials and energy has provided added incentive to reduce pollution by recovery of wastes for recycling or reuse. These trends are illustrated mainly by examples from the chlor-alkali industry (the manufacture of chlorine, caustic soda, sodium carbonate and related chemicals), for this is the area in the manufacture of inorganic chemicals where there have been recently the most significant developments arising from environmental considerations.

Experience with the discharge of mercury in effluents for chlor-alkali plants and the use of sodium polyphosphate in detergents illustrate the complex environmental problems which can arise from the manufacture and use of even relatively simple inorganic chemicals.

Recent developments in the recovery of waste calcium sulphate from the manufacture of phosphoric and hydrofluoric acids, probably the inorganic chemicals industry's most important single waste solids disposal problem, are briefly discussed.

Because of the trend towards stricter international controls on discharges to the sea and the non-biodegradability of inorganic chemicals, the siting of plants on estuaries or close to the sea will no longer provide such a convenient method of effluent disposal as in the past and there will be increasing need for improved effluent treatment and the development of less polluting processes. The stricter controls on disposal to landfill will mean a much more scientific approach to this operation than in the past.

In conclusion a plea is made for the use of cost benefit analysis to determine the allocation of the limited resources which can be devoted to improvement of the environment.

## 1. INTRODUCTION

The theme of the 2nd Congress is developments in measures to solve the problems of disposal of industrial wastes, both liquid and solid, which have taken place since the last Congress in November 1970. This period, which includes the 1972 United Nations Conference on the Human Environment at Stockholm, has seen great activity over the whole environmental field and the patterns established in this period will affect thinking and policy for some years to come. The aim of the present paper is to review briefly how developments in the inorganic chemical industries have reflected these general trends.

The illustrations in the paper will be taken mainly from the chlor-alkali industry (the manufacture of chlorine, caustic soda, sodium carbonate and related products) for not only has the writer been closely associated with this industry for many years, but this is the area in the manufacture of inorganic chemicals where there have been recently the most significant developments arising from environmental considerations.

The trends noted are:

(i) A greatly increased awareness of the need to protect the whole environment from harm by man's activities, whether these be the manufacture of products or their use by man.

(ii) A realisation of the finiteness of resources in energy and raw materials and hence the need to reduce the use of basic commodities by encouraging economy in their primary use and by the recycling and reuse of materials.

(iii) Increasing cost of manufacture resulting from increases in the cost of raw materials and energy and from the demand for more sophisticated forms of pollution control.

(iv) Efforts in large geographical areas e.g. the EEC and the USA to harmonise the philosophy of environmental control and the consequent legislation.

(v) The great proliferation of national and international groups with an active concern for the environment.

Concern is no longer confined to the effect of discharges from a manufacturing operation in the immediate vicinity of a plant, but extends to areas remote from the source of pollution and to the effects of the final product i.e. there is concern with total environmental impact.

## 2. THE BROAD APPROACH

Concern beyond the local point of discharge is illustrated by the Oslo and London Conventions which control strictly the materials which can be dumped into the sea. There is also a draft convention (the Paris Convention) to control discharges to the sea from land-based sources. These are the first steps on an international level to tighten the control of discharges to the sea which has for so long been accepted as an almost limitless sink for the disposal of wastes.

In the Oslo and London Conventions mercury is included in the 'black list' of chemicals, the disposal of which at sea is prohibited (except when present in trace amounts). Thus there is no question of using dumping at sea to solve the intractable problem of the disposal of solid wastes contaminated with mercury produced in the manufacture of chlorine by the mercury cell process. Mercury is also included in the "black list" for the Paris Convention, which could influence seriously regulations for the discharge of mercury in aqueous effluents even in situations where chlorine plants discharge to tidal waters or the sea.

Another industry which may be significantly affected by these conventions is the manufacture of cyanide. Considerable amounts of heat treatment salts containing waste cyanide are dumped in deep water beyond the continental shelf; this is currently acceptable under the conventions, but there are emotional reactions against this method of disposal. Cyanide is covered in the schedule of materials which require special care in disposal, and pressures may be exerted through this classification to restrict dumping at sea. Alternative techniques for disposal do exist, but they are in the final analysis expensive in energy. Limitations on the disposal of cyanide at sea could have an important influence in the development of alternatives to cyanide for heat treatment with a consequent adverse effect on the cyanide manufacturing industry. The need to present the scientific evidence that controlled disposal at sea is not environmentally harmful is a matter of importance for the industry.

The effect of these conventions on other inorganic chemical industries is more difficult to assess. Inorganic chemicals are usually not biodegradable, and a large part of the polluting chemicals discharged by the inorganic chemical industries into receiving waters will eventually find their way to the sea. In many instances the main constituent of the effluent will not be in the category of prohibited, or severely controlled, materials, but it will be important not to overlook the possibility that some of the minor constituents e.g. toxic metals, fluorides, may cause the effluents to be so classified.

The need for a broad, sophisticated but balanced approach to environmental problems rather than a simple parochial view is well illustrated by experience with mercury pollution in the chlor-alkali industry, which in recent years has been the most significant environmental problem in the inorganic chemical industry. For many years effluents containing very small amounts of mercury have been discharged into rivers and estuaries from mercury cell chlorine plants. This was no cause for exceptional concern since mercury in this form, and at the concentration in question, presented no greater hazard than a number of other trace components in industrial effluents. Laboratory work by Jernelov and others on the biological conversion of inorganic mercury in bottom sediments into the much more toxic methyl mercury seemed initially remote from large-scale manufacture of chlorine and caustic soda, but it did nevertheless raise the suspicion that discharges from chlor-alkali plants might result in some local environmental hazard such as local increases in the mercury concentration in marine life. Some evidence of this in North America was found in 1970. Under normal circumstances this would have alerted industry to the need to investigate the potential hazard more carefully and, if in due course it were proved necessary, to take appropriate action to reduce the amount of mercury discharged. Unfortunately, some years earlier there had been incidents in Japan where a number of people had been killed or seriously injured by eating fish with an abnormally high content of methyl mercury, probably the result of bio-accumulation of methyl mercury from effluents. The combination of circumstances led to a classical example of over-reaction and worldwide pressures for the imposition of strict controls on mercury discharges; the cost of meeting these standards in the chlorine manufacturing industry will be very large.

Despite exhaustive studies on the effect of mercury pollution, it is still debatable whether there is a need to

achieve the standards which are being suggested, particularly bearing in mind the natural occurrence of mercury in waters.

The environmental impact of products is probably the area of environmental concern where interest is currently increasing most rapidly. The inorganic chemical industry is fortunate in that the nature of its products are such that this is likely to be an area of less concern than in other sections of industry, such as the manufacture of pharmaceuticals or organic chemicals, but it is not without problems. There has been the claim that phosphates (as sodium tripolyphosphate) in detergents might be responsible for the eutrophication of inland waters in North America, which has led to regulations reducing significantly the polyphosphate content of washing powders in the USA and even to the suggestion that their use in such powders should be banned. In 1969, when the pressure to reduce phosphate in detergents was beginning to build up, production of polyphosphate in the USA was about 1.1 Mt/yr; the economic consequences of such a ban on the phosphoric acid and soda ash industries are obvious.

In anticipation of restrictions in the use of polyphosphate, manufacture of a substitute, sodium nitrilotriacetate, was established in the USA. Unfortunately, it was soon realised that the use of this material might also lead to environmental hazards e.g. the chelation and solubilisation of trace toxic metals in surface waters and also possible carcinogenic effects. The manufacture and use of the material in detergents has therefore been stopped. This again emphasises the need to avoid over-reaction to a potential environmental hazard—as the English expression has it “often better the devil you know than the one you don’t”.

There is also concern that nitrate derived from the use of inorganic fertilizers may add significantly to the nitrate in surface waters. As with phosphate, it has been argued that this contributes to the eutrophication of inland waters, but it is generally considered that except for a few localised areas this is not a matter of great concern. The more serious claim is that high levels in water are associated with a serious blood disease in infants and that it can lead to an increased incidence of some forms of cancer. Nitrate levels in water in some parts of the United Kingdom<sup>1</sup> have risen to the maximum recommended by WHO. It is of major concern to the manufacturers of synthetic nitrate fertilizers that the contribution of the use of fertilizers to these higher nitrate levels be reliably assessed before any controls are established. If controls are necessary they should at least be based on scientific appraisal and not on emotional reaction.

The inevitable consequence of a broader, more sophisticated approach to environmental problems has been the demand for more severe and wider controls on environmental pollution. Recent years have seen the transition from the situation where, unless the experts could provide satisfactory evidence of the effects of pollutants, their opinions were largely neglected, to one where there is a tendency to assume a hazard even when there is a minimum of evidence to show that such a hazard exists. The urgent need is for international cooperation between the controlling authorities and industry to agree reasonable standards based on a genuine scientific appraisal of the available data. It is tempting to take the easy solution and err largely on the cautious side by applying very strict controls, but the need to avoid unnecessary use of resources on pollution control is as pressing as the need to avoid waste of raw materials and energy.

### 3. CONTROL OF POLLUTION

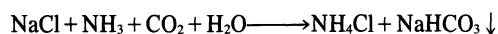
The great awareness of the significance of environmental pollution has brought with it a corresponding demand for improvement in the quality of discharges and better disposal methods. This can be achieved by:

- (i) Introduction of less polluting alternative processes.
- (ii) Improvement of existing technology to minimise the production of polluting effluents.
- (iii) Improvements in methods of treating existing effluents.
- (iv) Recycling and reuse of wastes.

#### 3.1 *Less polluting technologies*

Recent developments in the manufacture of soda ash from natural ash deposits is an example of a situation where an alternative technology has markedly reduced pollution. The basic chemistry of the ammonia soda process for the manufacture of sodium carbonate is such that the recovery of the ammonia for recycling leads to the production of 9 m<sup>3</sup> of aqueous effluent (containing about 10% calcium chloride, 5% salt and a small amount of ammonia) for each tonne of soda ash produced. Current world production of soda ash by the ammonia soda process is about 15 Mt/yr. Some calcium chloride is recovered from this effluent for sale, but despite considerable effort to find additional uses, the major part of the liquid effluent from the ammonia soda process is discharged to waterways or the sea. In North America, some of the ammonia soda process plants are on inland waters and undesirable pollution of these waters has occurred. Over recent years there has been pressure to reduce pollution from these sources and two plants on inland waters have been closed. The soda ash capacity thus lost, plus that required to meet the increase in demand, is now made from natural soda deposits by processes which do not have any significant liquid effluent problems. It is not implied that effluent problems are the only factor in the development of natural ash production—there were other important economic and technical justifications—but environmental pollution is a significant factor in hastening the decline of the ammonia soda process in the United States.

In Europe the situation is less satisfactory for there are no sources of natural ash and the large surplus of electrolytic caustic soda, which could have been converted into soda ash without serious effluent problems, has not developed as expected. There are alternative processes for making soda ash from salt which do not give rise to liquid effluent problems; thus it is possible to make soda ash and ammonium chloride from sodium chloride by the so-called "combined processes", the basic chemical equation for which is:



A few plants operating the "combined process" have been built in Eastern countries where there are fewer problems with the use of ammonium chloride as a fertilizer than in Europe or North America. The University of California<sup>2</sup> has developed a variation of the ammonia soda process in which ammonia and hydrogen chloride are recovered from the ammonium chloride mother liquor without the production of a large volume of liquid effluent. The ammonia is recycled and the hydrogen chloride is a co-product (which could be oxidised to chlorine). The writer knows of no full scale plant operating the process. To deal with pollution in Europe it has been necessary in

some situations to build very large reservoirs to store the effluent in dry weather, whence it is subsequently released at a controlled rate when the river flow is high.

A closely related problem is the disposal of the unwanted sodium chloride from the manufacture of potassium chloride in Alsace, which was formerly put in the Rhine. A number of countries bordering the Rhine are subsidising the stockpiling of this waste until a use or alternative method of disposal can be found.

Another example of the use of new technology to reduce pollution is the use of diaphragm cells rather than mercury cells for the manufacture of chlorine. In most of the world except the United States preference in the past has been for the use of mercury cells since it has been technically simpler and more economic to make high quality caustic soda and chlorine in mercury cells rather than in diaphragm cells. The pressure to reduce mercury discharges has inevitably led to increased capital and operating costs for mercury cell plants, and has given impetus to the development of more efficient and flexible diaphragm cell plants.

The costs of replacing existing mercury cells by improved diaphragm cells would be very large indeed; thus, for the United Kingdom alone, it would be about \$400 million (1974 prices). It is not expected that substitution of any major part of the existing mercury cell capacity will be done for many years in Western Europe. Currently, major replacement of mercury cells is only taking place in Japan where the authorities are proposing that about 50% of the existing mercury cell capacity shall be replaced by the end of 1975. Some replacement is taking place in North America. It seems highly probable, however, that throughout the world new chlorine capacity will largely be provided by diaphragm cells even though mercury cell manufacturers, motivated by the desire to retain the technical advantages of mercury cells (particularly the direct production of a concentrated pure caustic soda solution) have developed integrated designs for mercury cell plants which can be expected to have a very small mercury loss—it is claimed for the newest plants that the identified loss in liquid effluents should be less than 0.5 g per ton of chlorine, compared with 20/40 g for older plants of similar type.

#### 3.2 *Improved waste treatment*

For the major inorganic chemical industries it is not reasonable to expect expensive immediate replacement of existing processes by alternatives giving significantly less pollution. In the main, improvement will be achieved through improved methods of treating effluents from existing plants. In the inorganic chemical industries, the improvements will tend to be specific to the industry, but there are nevertheless a few generalisations which can be made. Many effluent streams are unsatisfactory with respect to pH (say, outside the range 5–9) and to suspended solids content. Technically, control of pH usually presents few problems; the problem is generally to provide a suitable neutralising agent at reasonable cost. Until recently it was thought that the development of a large surplus of cheap caustic soda would greatly facilitate the neutralisation of acid effluents since, unlike other alkalis such as limestone, lime or dolomite, there would be no problem with caustic soda with the disposal of precipitated solids such as calcium sulphate and of the unreacted residue of the alkali. Unfortunately, it now seems that a permanent surplus of cheap caustic soda for effluent neutralisation is not likely to be available for some years to come.

There have been some developments in the conventional methods to remove suspended solids from effluents containing a few hundred mg/l of such solids which are worth mentioning. One is the use of "tube modules" in conventional horizontal flow clarifiers; the effluent being treated is passed through an assembly of inclined passages on its way to the tank over-flow and this can result in a marked increase of the tank output. In one instance known to the writer the throughput was increased by 50%. The second is the development of techniques in which gas bubbles are induced to attach themselves to the flocculated solids and the floc is thereby floated to the surface and removed as an over-flow rather than an under-flow. Operation in this way is said to increase markedly the output from a given volume of sedimentation tank. In one form of the treatment the gas is generated in situ by electrolysis, in another by injecting water saturated with air under pressure through a special nozzle. A recent development<sup>3</sup> is the application of high gradient magnetic fields to remove finely divided magnetic solids from aqueous streams. The system can be applied to the normal run of materials, which are usually not magnetic, by incorporating recyclable magnetic particles in the flocculated solids.

In the ammonia soda industry the residual unreacted solids (from the lime) in the ammonia still effluents can be slurried in brine for disposal underground to worked-out brine cavities.<sup>4</sup> Formerly this was done by concentrating the solids in sedimentation tanks, filtering the under-flow, washing the filtered solids with water and slurrying the filter-cake in brine. Recently a technique has been developed whereby the slurry suitable for disposal can be produced in a single operation in the sedimentation tank i.e. the difficult and expensive filtration operation is eliminated.<sup>5</sup>

In this general review it is not proposed to consider developments in treatment techniques specific to particular inorganic chemical industries. It will be sufficient to mention that the areas of particular interest are the removal of mercury from chlorine plant effluents and the removal of ammonia and nitrate from effluents in the inorganic fertilizer industry.

### 3.3 Use of landfill

The inorganic chemical industries can produce directly or indirectly hazardous wastes e.g. mercury contaminated brine purification sludges from mercury cell plants, arsenic-containing wastes from separation plants to remove carbon dioxide from ammonia synthesis gas, cyanide residues from heat treatment shops. In the past, hazardous wastes were often tipped in any convenient hole without any great concern about the possible consequential damage to the environment e.g. pollution of ground water. Legislation aimed at greatly tightening control of such operations is either enacted or planned in many countries. Recent legislation in the United Kingdom (the Control of Pollution act 1974) has, for example, set even tighter controls on the tipping of hazardous wastes than existed under earlier legislation.

In future, the operation of tipping as a method of disposal will have to become increasingly more scientifically based. Companies offering facilities for tipping and manufacturing companies who tip their own wastes are beginning to use consultant hydrogeologists and other specialists to advise on site selection and management. The inevitable consequence of the increased concern over disposal to landfill sites will be pressure to find alternative

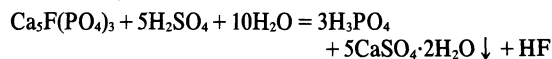
means of disposal. In the organic chemical industries incineration is often an alternative (albeit expensive), but this is not applicable in the inorganic chemical field; destruction of the toxic constituent by chemical treatment or recovery will be the more likely treatment.

The need to avoid contamination of ground water has led to the development of methods of minimising the extraction of toxic chemicals from landfill. Extreme examples (reported from Japan and the USA) are the incorporation of mercury containing residues from chlor-alkali manufacture into concrete blocks before disposal to landfill. Commercial processes are being offered using cheaper alternative binding agents, which are said to be applicable to a wide range of toxic inorganic chemicals.

### 4. RECOVERY OF WASTES

The widespread realisation which has developed over the past two years that the world's resources of energy and raw materials are finite has given great impetus to the conception of reducing pollution by recycling or recovery of wastes. The recovery and reuse of waste has, however, for many years been the serious concern of the inorganic chemical industries, and there have been successful examples of this in the past e.g. the calcination of waste calcium carbonate from the lime-soda process for the manufacture of caustic soda to produce usable lime, the use of some gypsum from the wet process for the manufacture of phosphoric acid to make plaster board, but despite considerable research and development work large amounts of materials are still wasted, e.g. calcium chloride from the ammonia soda process, most of the calcium sulphate from the manufacture of phosphoric and hydrofluoric acids. Recovery of materials involves energy and other resources and should only be justified if there is a genuine overall benefit to the community when all the factors are taken into account e.g. when the saving in raw materials and the disposal costs are carefully balanced against the use of energy and resources for recovery. It might be argued that in the future recovery will be favoured, because with depletion of resources recovered materials will become increasingly more valuable; unfortunately this is an over-optimistic view for the energy and resources involved in recovery are also becoming more expensive at the same time.

Probably the outstanding recovery problem in the field of inorganic chemicals is still the reuse of calcium sulphate from the manufacture of phosphoric and hydrofluoric acids. The manufacture of phosphoric acid from rock phosphate by the reaction



gives about 5 t of calcium sulphate residue per ton of acid produced; in the UK alone this amounts to about 2 Mt/yr. Despite the use of large amounts of natural gypsum in the manufacture of cement and plaster, only a relatively small proportion of the chemically produced calcium sulphate in the world is used in these manufactures. It is only used extensively where natural gypsum is scarce e.g. in Japan. Gypsum from wet phosphoric acid manufacture suffers from the defect that its impurity content varies depending on the source of phosphate rock and the differences can lead to significant differences in cement and plaster made from the waste gypsum. Since in most large phosphoric acid manufacturing plants phosphate rock from a variety

of sources is used, it is difficult to produce a consistent cement and plaster from waste gypsum. Processes for purifying the gypsum to give a consistent product have been worked out.<sup>6</sup> Gypsum is converted in an autoclave under carefully controlled conditions of temperature and concentration to give  $\alpha$ -hemihydrate and the impurities are mainly left behind in the mother liquor which is separated in a continuous centrifuge. The centrifuge cake can be used without drying to prepare high quality plaster castings e.g. blocks for partition walls made to such close tolerances that they need no further treatment before painting.

Because of the improved plasters which can be made from purified gypsum there is some current interest in the purification process, but it seems unlikely that any major part of the chemical gypsum available will be used in the manufacture of normal conventional plasters for some years to come.

There is a problem in the manufacture of plaster from by-product gypsum from phosphoric acid manufacture which well illustrates the complexities which can be encountered in developing what otherwise seems to be a straightforward recovery process. Plaster made from this gypsum has a higher radioactivity (derived from the radioactive impurities in phosphate rock) than most normal building materials. The UK National Radiological Protection Board has, however, concluded that the additional dose of radiation from the use of plaster made from the chemical gypsum is not likely to be significant, but if it is used to any marked extent the possibility of hazard from this source should be kept under review.

#### 5. COSTS OF POLLUTION ABATEMENT

This is an area where precise quantitative generalisations are difficult to make. The proportion of the capital costs expended on pollution abatement will vary greatly from industry to industry and within an industry will depend on local conditions. Furthermore, there is no generally accepted definition of what is covered by the costs; often the expenditure includes money which would in any case have been spent to protect the health and safety of employees and capital which could be justified, at least in part, by recovery of valuable products from effluent streams. On the other hand, no allowance is often made for circumstances where a more expensive but less polluting process is chosen in preference to a less expensive process. Some companies tend to emphasise the view that pollution control can often lead to substantial savings, but these savings rarely service the capital involved. Published figures usually suggest that industry spends up to about 10% of its capital on pollution control. The precise figure is, however, not important; what is important is that the cost of adequate pollution abatement is normally substantial, it represents a diversion of resources from other desirable activities and it is eventually paid for by the community at large.

Little has analysed the economic impact of the EPA proposed effluent guidelines for 24 inorganic chemicals (based on data supplied by EPA).<sup>7</sup> The economic effects were evaluated by assessing the likelihood that treatment costs would be defrayed through price increases and assuming that if price increases were not likely plant shutdowns would occur. It was concluded that mercury cell chlorine, lime, titanium dioxide (by the wet process) and sodium dichromate would be most affected.

#### 6. FUTURE DEVELOPMENTS

Weber, in the Plenary Lecture on the inorganic chemical industries in the 1970 Congress, suggested that there was the possibility of the sea as a disposal ground becoming increasingly important for industry in the future; current trends do not support this view. The stricter control of discharges to the sea will mean that industry must treat its discharges or develop a less polluting technology; the outstanding examples of this in the inorganic chemicals field are likely for some time to come to be the development of improved diaphragm cells and of techniques to remove mercury from the effluents from mercury cell plants.

The difficulty in obtaining landfill sites and the need to conserve resources will give impetus to the recovery of some wastes, but the writer cannot see any important advances in this area in the manufacture of inorganic chemicals. The use of by-product calcium sulphate is probably the most promising development.

The outstanding care in the future will be the need to be alert for the more subtle and unexpected forms of environmental pollution from effluent and products such as is exemplified by the discharge of inorganic mercury.

Finally, there is the allocation of resources to environmental control. It is not conceivable that there will ever be sufficient resources to make all the improvements in the environment which seem desirable at any given time. The question is how should the resources available be allocated between the various industries and between the various fields of pollution control (water, land, air). So far there have been few attempts to study this problem systematically in terms of some form of cost benefit analysis. If the limited resources available for improvement of the environment are to be used to best advantage the need for such studies is urgent.

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