Pure & Appl. Chem., Vol. 45, pp. 171–174. Pergamon Press, 1976. Printed in Great Britain.

TOTAL RECOVERY: THE FINAL SOLUTION OF WASTE PROBLEMS IN THE METAL FINISHING INDUSTRY

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Abstract—A systematic decontamination of industrial wastes and waste waters was started only after World War II. Research in this field seemed to provide suitable treatment processes for the wastes. As the water shortage problem developed, it was overcome through the development of ion exchange technology which brought a series of other advantages; but two disadvantages became apparent: the toxic chemicals absorbed from the water have to be eluted and treated in a separate plant; and additionally, the salt discharge to the environment was considerably increased.

Political and environmental developments in the field of water supply and management brought unexpected new recommendations. As the allowable concentrations of heavy metals are reduced, the salt content of the waste waters is considered more and more. In the USA, the Zero Discharge goals were decreed, and in the German Federal Republic, the remaining metal and salt content of the waste waters is to be taxed to an extent that may become ruinous for plants. Specialists doubt whether the requirements of these new laws can be met.

Our treatment technology is based logically on the elimination, or at least reduction, of the treatable chemicals and precipitation of metals. We are forced to recognize that the neutral salts and other untreatable chemicals are also pollutants. Down river communities have to use the polluted water from upriver industries for drinking, recreation, and agricultural purposes.

These developments require reorientation of our thinking. To reduce chemical consumption, ion exchangers have to be used more critically than is being done today. The integrated waste treatment system allows extremely low toxic residuals in the waste waters without increased chemical addition.

The most important future aims are: improved rinsing technique, modified processes taking account of the waste treatment requirements, segregation of the waste streams facilitating metals recovery, and the use of physical processes, such as evaporation and reverse osmosis. In particular a combination of these processes will gain additional importance.

Concentrates are especially harmful and have to be treated with great care. Exaggerated demands regarding the chemically treatable metal content are not practical and can provide no environmental benefit, but only high costs to industry.

1. INTRODUCTION

It is no longer necessary to discuss the importance of environmental protection to ensure the survival of the human race. One of the most important problems in this field is the elimination of solid, liquid, or gaseous waste products generated in industrial processes.

Industrial wastes vary much in their composition and in their toxicity. Among the most dangerous wastes are those of the metal processing industries and above all, those of the metal finishing industry. These issues will now be discussed.

2. HISTORICAL SURVEY

Until the beginning of World War II, industrial solid wastes were generally deposited anywhere without regard to soluble toxic content, and waste waters were discarded without preliminary treatment. It was believed that the dilution in sewers or natural waters was sufficient to eliminate dangerous effects. A simple calculation shows that in most cases this was not possible. The huge quantities of water needed for dilution are too expensive or not available.

It was only due to the relatively low degree of industrialization that no catastrophic effects were apparent. After the war, the industrial explosion caused damages that could no longer be overlooked. The first processes for waste treatment were developed and used on an industrial scale for the treatment of cyanides, the most dangerous chemical used by the industry. The toxicity of heavy metals had also to be taken into account. The studies on their precipitation in the form of insoluble compounds showed that the situation was more complicated than had been expected.

Methods have been developed which allowed the removal of the metals from the effluents to residual concentrations as low as several ppm. As a rule, the metal hydroxides have been settled and removed from the clarifier in the form of liquid sludges containing only one or two percent of dry solids. The high cost and danger connected with the disposal of liquid sludges aided the development of sludge filtration equipment or even pressure filters to replace the clarifier. The ability to filter solid sludges with 30–50% dry solids content made it easier to transport and to deposit these solid wastes. Nevertheless, the problems are not solved by these means. Less and less suitable area remains available for metallic sludges, and their uptake through the root system of the plants remains an environmental hazard.

3. RECOVERY OF WATER BY ION EXCHANGERS AND OTHER PROCESSES

When in the fifties we could assume that the metal industry effluents were treatable to a fair degree, another problem became more and more urgent and that was the increasing shortage of water. In industrial centres shortages have developed and the cost of water has increased so that the recovery of used water was inevitable. We may say that the ion exchangers have brought help at the last minute. Water softeners have been used for decades to get pure water for boilers, but they were not suitable for the purification of industrial effluents. The opportunity was provided by the development of the organic exchanger resins. These were used first by the late Dr. Furrer for the decontamination of waste waters. Soon it was found that the purification of effluents can be carried to such a degree that the water can be reused. Instead of using fresh water, the waste water was regenerated in a purer condition than was available from the mains. The use of ion exchangers in waste water technology ceased to be a luxury; the high cost of the exchangers was compensated by savings in fresh water and sewer charges.

Improvements of the resin qualities with regard to chemical and mechanical stability and an improved technology enabled the triumphal march of the ion exchangers in Germany in the early sixties. The ion exchangers made it possible to reuse 90% and even more of the water, reducing both the purchased water and effluent volume to 5–10% of the earlier practice.

Another important advantage in many cases is the possibility of producing, on a large scale, water of a purity unknown up to then which was needed above all in electronics, but also in other industries. To enumerate all the advantages of ion exchange technology would go beyond the confines of this lecture.

The success of water recirculation using ion exchangers stimulated the improvement of other processes also. Above all, the process of direct decontamination likewise enabled an extensive reuse of water. In the English speaking countries, these processes are called integrated systems, whereas on the continent they are known as the Lancy process. Processes such as batch treatment and continuous treatment in connection with filtration allow the reuse of water to a lesser extent.

4. DISADVANTAGES OF ION EXCHANGERS

Though ion exchangers have been extremely useful with regard to reuse and the purity of the water, they have two serious disadvantages. The one is that they only absorb and store all dissolved salts and toxic chemicals, but these substances are not destroyed; they have to be resolubilized during the regeneration and then chemically treated in a separate plant. The second disadvantage is the formation of large quantities of salts which have to be discarded with the waste water. By the direct precipitation of an equivalent of a heavy metal, one equivalent of salt is produced. By the use of ion exchangers, theoretically the double quantity of salt is produced compared with direct precipitation. For the regeneration of the cation exchanger, large excesses of acids are necessary and therefore additional quantities of salts are formed.

Earlier, when salts of alkali metals and alkaline earth metals were considered to be harmless, this was of no concern, but these times are gone and we have to change our thinking.

Improved technology such as counter-current regeneration, continuous moving bed ion exchangers, and other improved systems allow a considerable salt reduction, but even in the most favorable case, we have more than double the salt compared to precipitation without the exchangers. We must also remember that the improved ion exchanger technology requires very expensive plants, and the control and maintenance are also costly.

In the German Federal Republic the ion exchangers are often considered to be the best and most up to date processes for the solution of metal finishing waste water problems. It may be assumed that for the above reasons this opinion will have to be revised.

5. PROBLEMS IN CONNECTION WITH ANTICIPATED ENVIRONMENTAL REQUIREMENTS

We have to look at the whole complex situation of waste water, above all the purity demands of the public and the authorities in recent years. I have mentioned that until the sixties it was our belief that the degree of decontamination available at that time was sufficient for the protection of our natural waters and that the neutral salts of alkali metals could be considered completely harmless.

A radical change took place in the last decade. The rapid deterioration of our natural waters and the influence of an irresponsible daily press produced an environmental hysteria, and consequently, due to public pressure, drastic orders have been issued concerning wastes and waste waters, and even more regulations are to be expected.

As typical examples, the United States and the German Federal Republic should be mentioned. In the U.S., by 1985 the Zero Discharge goal is supposed to be reached, which means the elimination of all effluent discharges. In the GFR, from the coming year, effluents are to be taxed. The charges will depend on the volume discharged, solids content, and toxicity to fish and bacteria. Specialists are unable at this point to predict with any certainty the amount of the scheduled fees or how the requirements can be met. The law has been enacted and is in force, and industry will have to live with it. Until 1976 the law could not be enacted, but it will come one day.

The degree of treatment required by the authorities is within the region of the theoretically available minimum value. For instance, the allowed content of heavy metals is near the value of the solubility of the hydroxides. A significant improvement cannot be expected by the known practical methods. The addition of dilution water would diminish the concentration, but with regard to the total chemical load discharged to the environment, there is no gain. In view of the increased cost and prohibitions in most countries, the use of dilution water is not a feasible approach.

The only question that remains is whether there are not chances to improve the quality of the effluent and to reduce the pollutional load by a significant reduction and even elimination of the practice of the discharge of certain wastes.

To reply to this question we first have to think of the processes today in use and we have to take into account other known processes which have not been used for technical or economical reasons. The changed situation may favour such processes, and in many cases they may have been or can be improved remarkably.

It is necessary to call attention to widely spread abuses. For instance, the Statistical Federal Office of the GFR in Wiesbaden states that in 1967 the whole industry of the country discarded 10·6 billions m^3 of water, 1·1 billions m^3 of which were contaminated and discharged without any pretreatment. We can see that even in the GFR, a leading nation with regard to waste water treatment, a large part of the polluting effluents are discharged without treatment. It does not make sense to improve the purity from ppm to ppb of some effluent when at the same time kilograms and tons of impurities, or even poisons, are discharged.

It was stated that in view of additional salt generation, ion exchanger installations have to be regarded much more critically than usual. It is damaging when in a large plant all water needed is taken from ion exchangers even when the high purity is unnecessary. A segregation of the water supply system seems to be useful even though the investment may be considerable. Processes requiring the purest water connected to the ion exchanger, scarcely contaminated or tap water for ordinary use, and contaminated water for selected rinses and non-critical processes.

We believe that in the water supply arrangement, we will utilize the ion exchangers, but they have to be used where needed and in an economical way, considering also the environmental requirements, and not just on principle.

6. THE INTEGRATED WASTE TREATMENT SYSTEM

The only process allowing exceptionally low metallic and toxic chemical residuals in the discharged effluent, is the integrated waste treatment system of Dr. Lancy. In this system the work piece taken out of the electroplating bath or processing solution is not rinsed in pure water which greatly dilutes the adherent toxic impurities, but the work is immersed directly in a decontaminating solution, the chemical rinse. In this way the initial dilution of the impurities is eliminated, the desired chemical reactions are accelerated, and are more complete. Normally the initial concentration of toxic substances in the adherent solution film on the work is 10–100 g/l and is reduced by rinsing nearly 10,000 fold. In the integrated system, the remaining concentration after the chemical rinse is in the range of mg/l. and is then additionally greatly diluted in the subsequent water rinse to final concentrations at the ppb level. This water, since it contains no toxic substances and is low in salt content, is recycled and only 5–10% is discharged to avoid salt build-up. Of course, the recycled water is not purer than the fresh water, but where pure water is needed, fresh water or desalted water from ion exchangers can be used. The fresh water used before entering critical processing baths serves as blow-down for the reuse water that is recirculated and is usually 5–10% of the total water recycle volume. The reduced chemical consumption for treatment and the use of a segregated, recirculated chemical rinse, allow a 90% water recycle without any chemical consumption, and thereby increased the salt content of the discharged effluent.

7. HOW TO AVOID THE GENERATION OF WASTES

7.1. *Improved rinsing technique*

Fundamental mistakes can be found in the rinsing technique, We cannot discuss this question in detail, but the multistage cascade rinse can avoid the discharge of an effluent altogether. The method is not always practicable, but in many cases it can contribute to a reduced consumption of water and hold the waste generation to a minimum. The reduction of effluent volume inevitably leads to a reduction of all problems and costs connected with waste treatment. It cannot be emphasized enough that a correct rinsing technique is always the first step to save valuable raw materials and to avoid the formation of unnecessary wastes. In an existing plant, it is probably difficult to improve rinsing by adding new rinsing stations, but in a few years this will be the necessary procedure.

A difficulty in the way of total recovery of all effluents is the increasing contamination of the processing solutions by products of decomposition and drag-in of undesired substances. An intermediate purification by small ion exchangers can be helpful. Nevertheless, in many instances, the total avoidance of wastes by an appropriate rinsing technique cannot be provided and a reduced quantity of wastes will have to be treated.

We have to consider that in the future, the discharge of waste waters containing any dissolved or suspended substances could be either prohibited or charged with exhorbitant fees. How can we escape this situation?

7.2. *New methods of cyanide treatment*

Sometimes existing processes can be considerably improved, as for example the elimination of the most toxic chemicals in use, the cyanides. Cyanides are oxidized by gaseous chlorine or hypochlorite, and all chlorine added in any form to the waste is finally present in the effluents in the form of chlorides. Recent studies have shown that the oxidation can be performed in many cases with hydrogen peroxide or ozone. Electrolytic oxidation methods are already applied very well for concentrates. Recirculated electrolytic treatment, regenerating the salt used for chlorine generation, can likewise be useful to reduce the consumption of the oxidizing chemicals. The advantage lies in a radical lowering of the salt load to the environment.

7.3. *Segregation of waste water streams and metal recovery*

In the integrated system the chemical rinse solution has to be renewed from time to time. It contains the precipitated heavy metals in the form of hydroxides. Though it is possible to treat different metal solutions with the same chemical rinse, there is no difficulty in segregating these solutions and to recover the pure, unmixed hydroxides from each. The pure metals or metal compounds can be recovered without difficulty from the segregated metal sludges.

All other processes give only mixtures of hydroxides when different metals are coming from a mixed waste stream. It is difficult and costly or even impossible to recover the metals from these mixed sludges. In the future it may not be allowable to deposit metal hydroxide sludges and we shall be obliged to separate the waste water streams according to their metal content for the purpose of recovering the pure metal compounds. The recovery of the heavy metals will be required, not only for the purpose of recovering the metal values, but in order to avoid or reduce the generation of metal-containing sludges.

7.4. *Prevention or reduction of chemical wastage*

The heavy metal content of the effluents can be recovered totally with present technology, even though the expenditure may be high, but the remaining solutions always contain considerable amounts of salts. Several years ago no attention was paid to these salts in waste waters, but today we have to consider the total salt load discharged to the environment. The nitrates, chlorides, sulfates, phosphates, fluorides, and fluoborates are all pollutants and cannot be easily removed in waste treatment. Pollution is not only measured as mg/l content of the highly toxic substances, but also the overall pollution caused by these chemicals. The added nutrients, such as nitrate, phosphates, and ammonia, cause algal proliferation. All the chemicals impair the usefulness of the water streams for drinking water, recreational, or agricultural uses. With population growth and further industrialization anticipated, these issues have to be faced and our plans formulated accordingly.

It is obvious that the industry will have to focus on waste abatement. Instead of wasting chemicals, the emphasis will have to be on recycling and regeneration. With a different attitude on our part, and greater interest in processes with no waste generation, it will be found that many of the processes which we had thought uneconomical or not practical will become available and also economical considering the costs of water, chemicals, and sludge disposal difficulties.

Physical processes operating without chemical additions offer special advantages. One of these well-known methods is rinse water recycle by evaporation. Multi-stage vacuum evaporation of dilute rinse solutions is operated today advantageously. The drag-out solution is recovered in reusable form, and the water is recycled. When needed, the dilute solution can be purified by ion exchange before evaporation.

Another new process in waste water technology is reverse osmosis. In principle, it enables the separation of dilute solutions to a concentrate and pure water. The water recovered contains traces of salts but this does not affect its usefulness as recycled rinse water. The concentrate is returned to the process solution. From a technical point of view, the best approach would be to recover the rinse waters by reverse osmosis in segregated installations of individual units, one for each process.

The concentrate from the reverse osmosis units could be brought to the process solution concentration by evaporation. Today, for economic reasons, the reverse is done; that is, the concentration of the mixed eluates from the ion exchangers by reverse osmosis reduces the waste volume that has to be treated.

8. CONCENTRATES

The volume of the concentrates that are discharged is only a small part of the volume of the dilute rinse water effluents, but they contain about four-fifths of the total chemicals wasted. Therefore, the environmental load from these sources is the most severe. The old method of feeding the concentrates in small doses to the rinse waters is no longer practicable. The concentrates are best treated separately. For this purpose, central plants are most useful. The aim should be to discharge concentrates as rarely as possible. The concentrates should be maintained most carefully, and all methods of regeneration available should be utilized. Electrodialysis can offer useful help and may provide almost unlimited service life to chromate-containing solutions. When the discharge of concentrates cannot be avoided, the heavy metals have to be eliminated, and if the anions can be rendered insoluble, such as with calcium precipitation, the total chemicals discharged to the environment could be limited.

Special problems arise with spent pickling solutions for iron and other metals. Only for large plants is it possible to recover the acids and iron oxide so that no wastage occurs. Even smaller plants can regenerate their copper and brass pickling solutions through the use of electrolytic or crystallizing-type maintenance processes. Sulfuric-acid-type pickling solutions at least provide the advantage that the anion can be immobilized by lime neutralization.

9. CONCLUSIONS

We have discussed waste water treatment processes that allow the recovery of the heavy metals as well as the water. The generation of sludges which have to be filtered and deposited can be prevented in many instances.

It is always possible to improve the rinsing technique; the higher cost will be offset with reduced waste treatment and reduced chemical load in the discharge. The recovery of heavy metals is made possible by segregating the rinse waters according to their metal content. Ion exchangers must not be used indiscriminantly. They are indispensable for the production of purest water; they are very useful for the recycling of water, but they are not the best answer for metal finishing waste treatment from an environmental standpoint. The increased salt loading should be taken into account. This disadvantage can be eliminated to a certain extent by combining them with physical processes such as evaporation or reverse osmosis for drag-out recovery ahead of the desalted, recirculated water rinse.

The future of waste water treatment seems to be in the judicious use of a combination of various processes and equipment in the waste treatment installation design.

The solutions with high content of salts after neutralization and the precipitation of the heavy metals can be processed to solid residues, but we have to consider that the evaporation and crystallization require disproportionate quantities of energy. Such a dissipation of energy is more harmful than the discharge of low quantities of carefully treated solutions. Considering the tons of salt used for snow removal from our roads in the winter, the environmental load from these wastes may be minimal.

It is technically possible to have an absolute zero discharge, but the cost of this is much too high and poses new, unknown hazards for environmental contamination. The final solution of the waste water problems will not be the observance of an absurd principle, but the acceptance of a reasonable compromise that guarantees effective protection for our environment without excessive energy consumption and unnecessary additional costs to the industry. It is most important that the various governments listen to the scientifically and technically trained and experienced leaders of the industry to realize what the available options are before the enactment of potential technically unsound regulations.

It was not possible to discuss all the potential variables and problems regarding this subject as, for instance, complexing agents, wetting agents, and other important topics, in view of the limited time available for this report. I hope to have given a brief survey of our present problems, the tasks ahead of us, and the ways that we will have to progress to overcome these problems.