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PRE-TREATMENT AND ELIMINATION SYSTEMS OF TOXIC INDUSTRIAL WASTE AND SLUDGES. THE CASE STUDY OF THE DEPARTMENT OF ATTIKA

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ABSTRACT

In the departments of Attika and Viotia there are about 1,100 industries. The total amount of produced waste from the above mentioned branches is 20 x 10^6 t/year, 600,000t of which contain toxic substances. By contract from October 1st, 1992 between the Ministry of the Environment, Regional Planning and Public Works and three collaborating offices (among them the office of C. Malliaros) has been assigned to the latter, the realisation of a study of the management of toxic waste (liquid) and sludges, in the Departments of Attika and Viotia. The study presented in this paper investigates the following: - collection and evaluation of data and estimation of the hydraulic and pollution loads - classification of industries according to sewage facilities - further possibilities for changes of improvements in the production process of the industrial branches for the reduction of pollution and representation of these industries on maps - proposals for the collection and transport of the liquid toxic waste and sludges - pre-treatment at the source and disposal of the liquid waste and sludges - presentation of administrative and legislative regulations - forming a policy for the management and monitoring of this waste - technical and financial evaluation and investigation of the alternative methods of treatment - suggestions for the development of the area concerning the activities and the expenses at various levels. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Classification; collection; disposal; elimination; financial evaluation; pre-treatment; sludges; toxic waste.

INTRODUCTION

In this research the existing data of the following industrial activity in the area of Attika and Viotia is recorded: dye-works, tanneries, industries producing lead accumulators, coating metals industries, industries with oil residues, basic metals industries, chemical industries. The seven industrial branches are investigated with the following sources: Register of Industries, industrial section of Public Power Corporation, recorded data from studies and researches, Ministry of Industry, control programme for industrial liquid waste and sludges from the Prefectures of Attika and Viotia. The collected data, of the seven toxic branches above mentioned were introduced into a computerised database. The database was installed on Windows 2.1. and has the following properties: introducing the data, classification - search of the data (detailed lists per serial number, per code of activity and partial lists, per code of activity and combination of classification). All the collected data are depicted at a map scale 1:10,000 from the maps of the Geographical Military Service.

Dyeing and finishing industries. The waste originating from dyeing units is mainly liquid and varies in quality and quantity. The dyes containing metals are soluble and this makes even more difficult their removal from the waste. Sedimentation is not successful and for that reason adsorption or ion exchange is required. Other problems are those of oil concentrations. The produced liquid waste in a dyeing-finishing unit has significant fluctuations (EPA, 1979).

Tanneries. In Attika there exist many small tannery units that are scattered and often found in residential areas causing acute odour problems. Only in a few cases there exist elementary treatment units of which the treatment capacity is considered doubtful. The tannery wastes vary in toxicity on account of their chromium content. Waste from tanneries contains organics (proteins, amines, saccharides, starch), CaO, $CaCO_3$, CaS_2, sand, hair, fat, oils, etc. The BOD_5 and COD concentrations are especially high and this is due to the presence of hairs and blood. pH is acidic and the suspended solids are found in high concentrations and they vary between 100-700 mg/l.

Industries producing lead batteries. In the area of Viotia there is only one very big unit with such an activity. The liquid waste originating from units producing lead batteries is a very toxic waste, given that it contains lead and sulphuric acid. The waste produced by the industries producing Pb accumulators is acidic (pH=3) and contains both dissolved and in suspension Pb and SO_4^{-2}. Table 1 presents another estimation of qualitative characteristics of these industries.

Table 1. Qualitative characteristics of waste from industries producing Pb accumulators

Parameter	Concentration
Pb	10-60 mg/l
SO_4^{-2}	2-10 mg/l
Precipitated	10 mg/l
pH	3
Waste supply	1-5 m^3/t Pb

Metal plating industries. The metal plating units produce little but very hazardous waste due to their toxicity. The most significant toxic pollutants are acids, and heavy metals such as Zn, Cr, Ni, Sn as well as cyanides. Also alkaline cleaning agents, lubricants, and oils are traced in the waste. The most toxic constituent of the metal plating waste are the cyanides which have lethal effects on humans. Besides, the metal plating cleaning wastewater is dangerous to the sewage network, the cleaning installation and obviously to the receiving water bodies too. It is therefore obvious that especially the toxic ions CN^- and Cr^{+6} should be removed from the waste regardless of the cost, either with chemical or biological methods, prior to any treatment of the total volume of waste. The qualitative waste characteristics vary significantly according to the metal plating conditions (anodes used, rinsing method etc.). The pH value varies because the alkaline-cyanide baths are basic, whereas the chromates are acidic. The organic load of waste is mainly due to oils. The suspended solids consist of the dissolved metals and the solidified paints which originate from the metal plated surface. Finally the heavy metals have a greater variation due to the aforesaid reasons.

Industries with oil residues. The regeneration of used lubricants is an industrial procedure which, although it saves natural resources (mineral oils) and consequently abates adverse environmental impacts from the useless rejected lubricants, it constitutes a significant source of toxic waste. The temperature of liquid waste from industries regenerating lubricants is in accordance with the permission limits, because even though their initial temperature is high, it is reduced when they are introduced in the oil separator (API). When refining with H_2SO_4, acidic sludge is produced and consequently pH is far away from being neutral. H_2SO_4 amounts to 40% by weight in the acidic sludge. Additionally the waste contains a significant quantity of oils and phenols.

Basic metal industries. The basic metal industries include certain industrial units producing and treating metals and their productive activity is directly involved with the production of liquid, toxic industrial effluents and sludge. This group consists of the following industrial activities: steel industries, industries treating and processing metals, shipyard industries, ship dismantling industries, units producing air-conditioning equipment and central heating equipment, units producing domestic electric appliances, units producing tin cans, units producing chassis of trucks, cars and buses, lead metal works. The pH values in the production of building grid activities range between 7-8.5. The COD values are low: less than 10 mg/l. The suspended solids range between 10-50 mg/l, this is due to substances that stick on the metal surfaces and which are removed by sprinkling the metal surface with water. The oil values are low: less than 10 mg/l. The metals found in the waste come mainly from the scrap and the additives. Thus, all the metals are in concentrations less than 0.1 mg/l except for iron which ranges between 2.5-4.5 mg/l. In the case of metal processing and treatment, toxic waste is produced only if the treatment includes metal plating (M.E.P.P.P.W.-Part VI, 1987).

Chemical industries. The main industrial activities directly involved with the production of toxic waste which are examined are the following: industries producing acids, bases, salts and fertilisers, industries producing artificial fibres (silk), industries/manufacturing units producing paints and synthetic resins, industries/manufacturing units producing insulating materials. In Viotia, there are two industrial units producing insulating materials, one of which is one of the biggest units of the branch. In addition there are thirteen industries/small industries producing paint/dyes. In Attika, there is only one unit producing fertiliser with simultaneous production of acids. The treatment of liquid waste from industries producing acids and fertilisers results in the production of large quantities of toxic sludges which are disposed without any pre-treatment. An additional problem is the disposal of sludge originating from the treatment of liquid waste coming from the industries producing artificial silk, which contains toxic metals. The liquid wastes produced in the paint industries are not toxic but have high COD loads which imposes their biological treatment prior to their discharge to the sewage network. It is worth saying that the most acute problem of this branch is the air pollution caused by the release of significant quantities of volatile organic solvents used for the production of paint and varnishes. Finally, the waste of industries producing insulating materials have limited toxicity and do not present a serious environmental problem. The waste originating from units producing H_2SO_4 are mainly cooling waters and waters from exhaust gas cleaning which cause insignificant pollution. The waters from the production of HNO_3 contain HNO_3 (3000 mg/l) and few inorganic salts. During the production of H_3PO_4 solid waste mainly containing gypsum is produced. Phosphorus and fluoride are the main pollutants and should be removed. Typical qualitative and quantitative characteristics of waste are presented in Table 2.

Table 2. Qualitative and quantitative characteristics of waste from the production of fertiliser

Parameter	Cooling water and water from gas cleaning	General
COD	–	100 mg/l
$N(NH_3)$	–	100-200 mg/l
$N(NO_3^-)$	–	90-180 mg/l
SS	60-10 mg/l	230-900 mg/l
SO_4	–	200-500 mg/l
CO_2	30-90 mg/l	–
H_2S	12-15 mg/l	–

The waste produced during the production of artificial silk is mainly acidic and contains sulphur in concentrations up to 100 mg/l in the form of C_2S, H_2SO_4 and insoluble organic compounds in concentrations ranging between 100 mg/l-1 g/l. Table 3 depicts the waste characteristics from paint industries.

Table 3. Qualitative and quantitative characteristics of units producing paints

Parameter	Value (ppm)
pH	6.9
BOD_5 at 20°C	470
COD	3,980
Total organic	2,370
Calcium	68
Titanium	>2

From the above table it is obvious that the waste has high COD values, and these values do not permit their disposal without prior treatment. The wastes from the production of synthetic resins contain phenols, formaldehyde, oils, acids, polyoles, and suspended solids. Consequently they have high BOD_5 values and pH=3. The wastes originating from the production of polyurethane foams contain many organics (polyoles) and for that reason their biological treatment is required. Toxic sludge is not produced. The waste produced from polystyrene production is not toxic.

IMPLEMENTATION OF MEASURES REDUCING INDUSTRIAL WASTE AT SOURCE

Prior to employment of measures for the management of industrial waste, it is an absolute condition to take measures for the reduction of waste water and sludges produced. As has been previously mentioned, these measures can consist of some simple process changes or even some more complex ones concerning the technology applied. The proposed measures for the industrial activity in Attika and Viotia are listed in accordance to the registration.

Dye works. There are 132 dye works in Attika. They process about 60,000 t/year of textile fibres (M.E.P.P.P.W.-Part IV, 1987). On average, one company processes 2 t/day. The size of companies varies much. More than half of the companies are very small or small. They process less than 1 t/day. Only a handful of companies process more than 5 t/day and may be called bigger companies. The rest of them are medium sized. On average, one ton of processed fibres leads to the generation of 214 m^3 waste water.

One-bath-process. In non-continuous processes, the AOX generation of the combined bleach (peroxide plus hypochlorite) can be minimised by working in one bath. The fibres stay in the bath of the hypochlorite bleach, caustic soda is added and after 10-15 minutes the peroxide is added. This measure leads to 80% less AOX.

Big companies. Most of the measures described before could be applied here, too. In some cases, more sophisticated measures seem to be adequate for a bigger company as listed below.

1. Recovery of sizing agent. 2. Substitution of chlorinated bleach. 3. Optimising the rinsing technology. 4. Recycling of alkali. 5. Reuse of dyeing baths. 6. Reducing the volume of trough. 7. Filtering of printing pastes prior to adding the colour. 8. Mechanical pre-cleaning of printing paste containers. 9. Computer-aided printing paste recycling. 10. Reducing the use of urea in the printing process.

The application of the above measures allows a reduction of waste water load from 214 m^3/t to 140 m^3/t of product.

Tanning: small companies. There are 122 companies in Attika which produce about 4,000,000 m^2 of leather per year. There are four big plant estates, with the others being rather small. The biggest plant produces about 600,000 m^2/year of leather (M.E.P.P.P.W.-Part V, 1987).

Measures to reduce water. Batch water instead of running water, reduction of excessive water consumption, soaking and liming in one bath, tanning in higher concentrated baths, exact mixing of chemicals.

Measures to reduce toxic substances. Avoiding the application of pesticides, substitution of dangerous pesticides, avoiding chlorinated products, application of ammonia-free deliming and bathing agents, avoiding metal complex dyes, separating organic residues from the waste water by a sieve.

Medium sized companies. Some companies have less than 20 employees. They are mostly operated by families and produce between 50,000 and 100,000 m^2/year. The cost of internal measures for small and medium companies must not exceed 1-2% of the volume of trade. In general, the best concept would be to develop single concepts for the avoidance and reduction of waste water in every single tannery which includes the individual character of each company. The individual concepts belong to a general concept (see above proposals) which should be applied in all companies. This concept should be part of a programme of rationalisation measures, process technology replacement and meeting of the ISO 9000. The final costs of this concept would only relate to acceptable environmental standards.

Big companies. The four biggest companies have more than 20 employees and produce more than 100,000 m^2. All measures which are described for smaller and medium companies should also be applied here. Moreover, they could do the following:

Checking of the recipes. All the applied chemicals should be checked first - if they are hazardous, alternatives should be sought. As a result chlorinated compounds, heavy metals etc., are either avoided or reduced.
Chromium recycling. This measure is already applied in a big tannery and has brought very positive results. Every big tannery should consider to apply chromium recycling. A 25% reduction of the wastewater at source is achieved.

Electroplating. There are about 150 electroplating plants located in Attika. They employ in total about 1000 employees. The units can be separated into very small ones (<3 employees) and small ones (3 to 15 employees). Up to 45% of the facilities apply chromium baths, 20% have cyanide baths, and 20% cadmium baths. On average, about three rinsing steps are included. A total amount of about 3000 m^3/day of waste water is produced. None of the companies has a wastewater treatment plant (M.E.P.P.P.W.-Part II, 1987).

Very small factories. For all the baths the following is proposed: 1. *Increasing the number of rinsing steps,* which requires new equipment (e.g. stationary rinsers, flow rinsers, etc.), 2. *Reducing the concentration of the coating baths,* 3. *Sufficient dripping time,* 4. *Except chromium baths: recycling of rinsing water.* The losses of the coating baths which are caused by spreading and evaporation (particularly in the hot baths of copper cyan and nickel) can be compensated by adding water from the stationary rinsers, 5. *Chromium only.* Stationary rinser with bisulphide for decontamination. Enough space for new bath containers is required which is disadvantageous. As a result, the sum of waste water is reduced to about 250 m^3/day. 10-20% of valuable substances could be recycled. The decontamination of chromium would be integrated in the process, while cadmium and cyanide contaminated waste water has to be treated externally if necessary.

Small factories. In addition to these measures for very small factories the following can be applied 1. Resharpening of pickling baths, 2. For copper cyan and nickel: filtration of the bath with filtering candles or activated carbon filters, 3. For nickel: invention of a local ion exchange circuit.

Conclusion. The application of these measures reduces wastewater from 3,000 m^3/day to 1,250 m^3/day i.e. more than 50%.

Viscose production. As the cooling water is taken directly from the sea, no reduction measure seems necessary.

Conclusions. The measures discussed are the most suitable ones considering the existing industrial activity of the examined branches in the regions of Attika and Viotia. The reduction of the wastewater hydraulic loads for every branch proves their effectiveness and the need for immediate implementation. In Table 4 the estimated hydraulic loads of liquid waste per branch before and after taking the measures, are summarised.

Table 4. Estimated hydraulic loads of liquid waste in Attika-Viotia before and after the implementation of measures for waste reduction at source

Branch	Liquid waste (millions m^3/year)		Reduction
	Before	After	
1. Dye-works	14-17	8.2-10	~40%
2. Tanneries	0.75-1.2	0.5-0.8	~25%
3. Plating-works	0.75-0.9	0.375-0.45	~50%

The table shows the results brought about after the implementation of the measures for waste reduction at source, and their importance.

PRE-TREATMENT OF INDUSTRIAL LIQUID WASTE

This involves primary or mechanical treatment of the waste which includes screening, separation of other floating solids (preliminary treatment) and primary sedimentation together with the necessary sludge treatment. In each branch the necessary inplant pre-treatment works are suggested taking into account the existing treatment facilities and the quality of produced waste water. A brief description of the works per branch follows:

Screening, skimming tanks, with a fat separation following, mechanical cleaning neutralisation, primary sedimentation-flocculation, sludge concentration-filtration, finally, flow equalisation is necessary to equalise the pollution load.

Dyeing-finishing works. It is estimated that 85% of the liquid waste of the wastewater load of a dye works comes from the discharge of rinsing baths while the other 15% comes from the discharge of concentrated baths (baths with dye floats) (Markantonatos, 1990). These baths have high AOX content, non-biodegradable compounds and high COD values. It is thus estimated that 85% of the total yearly liquid waste hydraulic load must undergo inplant pre-treatment. Taking into consideration that approximately 60% of the dyeing-finishing works have wastewater treatment facilities such as screens and sedimentation tanks, it is estimated that inplant treatment of the wastewater is necessary for approximately 53 industrial units. Inplant treatment should include screening - flocculation - neutralisation - sedimentation - sludge concentration. Regarding that 25% of the dye works - mainly medium and big - use biological cleaning, the discharged concentrated baths of the rest of the dye works (75% mainly small and medium) together with sludge produced from inplant pre-treatment, must be led to the central treatment plant for toxic waste cleaning. The hydraulic load of these concentrated baths is estimated at 500,000-600,000 m^3 of liquid waste yearly.

Tanneries. It is estimated that 50% of the liquid waste of the branch comes from the activity of small and medium tanneries, and that 5% of this load comes from the discharge of concentrated baths of chromium tanning. About 1/4 of the tanneries use collection and sedimentation tanks and only one recovers chromium. Inplant treatment will include screening - flocculation - sedimentation - equalisation. Most of the owners of the tanneries would be willing to move to a place outside Eleonas. As it seems impossible to find a place to accommodate the tanneries near Athens, and as the tanners do not want to be too far from their market in Athens, this solution, which has been discussed since the end of the 1960s is not feasible. A newer plan is to found a cooperative beamhouse outside Athens which will apply chromium recycling and wastewater treatment and which prepares wet blue for the bigger tanners.

Plating works. Almost all the plating works need to treat their waste inplant with the exception of the depleted metal baths and cyanide-cadmium baths which will be transported and treated in the central treatment plant for toxic waste together with the sludges coming from inplant pre-treatment. 150 electroplating units were registered of which the main characteristic is their small size. No treatment at all is realised in any of these. Consequently, inplant treatment must consist of neutralisation-equalisation which is problematic due to lack of space.

Production of artificial silk. There is only one industrial unit producing artificial silk (ETMA s.a.) in Greece which is located in Eleonas and already applies wastewater treatment inplant. The sludge can be transported to the central treatment plant. Given the fact that this sludge contains ZnS it has to be treated in the toxic inorganic sludge treatment part of the plant.

Paint production. 139 units were registered, 50% of which use recycling and solvent recovery. Solvents are used in the production of varnishes. The wastewater is treated in distillation plants which recovers solvents in order to reuse them in the production process. In about 50% of the units (about 70) inplant treatment for wastewater resulting from plastic paints production (PVA) is necessary. Only plastic paint production (PVA) leads to the production of wastewater because the used solvent in this case is water.

Lead accumulators production. Only one out of 31 registered plants in the study area uses water treatment. For the rest of the units inplant pre-treatment must include: neutralisation - sedimentation - sludge concentration. Finally for the rest of the branches no inplant pre-treatment is required.

TREATMENT OF TOXIC WASTEWATER AND SLUDGES IN CENTRAL TREATMENT PLANT FOR TOXIC WASTE

As has been previously mentioned the highest amount of wastewater with the exception of some concentrated waste which cannot be adequately cleaned, must be pre-treated inplant. This concentrated waste contains high concentrations of heavy metals, halogenated hydrocarbons, non-biodegradable compounds and high BOD_5 and COD values. For this reason, it must be led to the central treatment plant for toxic waste . Furthermore, sludges which originate from inplant pre-treatment must also also led to the central plant in order to be decontaminated. In Table 5 the estimation of the introduced amounts of wastewater to the central plant from Attika and Viotia regions are listed.

Table 5. Estimation of toxic wastewater and sludges of Attika and Viotia treated in the central treatment plant

Composition	Amount
Dye sludges	12,000-15,000 t/year
Tannery sludges	7,000-10,000 t/year
Paint sludges	450 t/year
Refinery sludges	6,000 t/year
Other oily sludges	4,000 t/year
(used oils regen. Shipyards)	10,450 t/year
Dyeing baths (floats) from dye-works	500-600,000 t/year
Cd, Cn- baths	40-50,000 m^3/year
Sludges from dye works, tanneries, plating and artificial silk production	80-110,000 m^3/year

COST OF INPLANT PRE-TREATMENT WORKS IN THE REGIONS OF ATTIKA AND VIOTIA

On the basis of the estimated inplant pre-treatment works in the region of Attika and Viotia, distinction is made between construction works and electromechanical works. Assuming that the operating maintenance and depreciation cost is 25% of the capital cost, the elements of the cost of pre-treatment appears in Table 6.

Table 6. Detailed cost account of inplant pre-treatment works at source in the region of Attika and Viotia

Cost of construction works	500 million DRS
Cost of electrochemical works	1,700 million DRS
Total capital cost	2.2 billion DRS
Cost of operation maintenance and plant depreciation	0.55 billion DRS

CONCLUSION

The study investigates the following:

A. The reduction of waste at source by means of applying new process technologies or updating the existing ones (Table 7).
B. The reuse of waste by means of treatment-recycling facilities.
C. The treatment and final disposal of waste with the least harmful implications to the environment.

The study consists of the following parts:

- Collection and evaluation of data and estimation of the hydraulic and pollution loads of industrial wastewater and sludges.
- Classification of industries according to sewage facilities.
- Marking of industries on maps.
- Collection and transport of toxic waste.
- Treatment and disposal of wastewater and sludges.
- Administrative and legislative regulations.
- Managing body and invoice policy for the management of toxic waste.
- Technical and financial evaluation and investigation of the alternative methods - treatment methods.
- Financial implications per industrial branch.

In the region of Attika and Viotia there are about 1100 industries of varying size which produce toxic waste (Table 8). The main branches are the following: Dyeing-finishing works, Tanneries, Production of lead accumulators, Plating works, Industries with oil residues (used oil regeneration, oil refineries, companies selling and distributing oil, shipyards, and ship repair works), Industries with basic metals, Chemical industries (production of fertilisers and acids, production of artificial silk, production of paints, varnishes, ink, and production of insulating material).

The total amount of produced wastewater from the aforementioned branches is 20,000,000 t/year, 600,000 t of which contains toxic substances and must be treated. Further, 500,000 t of the 600,000 t is the first dyeing baths from dyeing-finishing works and the other 100,000 is the wastewater from the remaining branches which undergoes inplant pre-treatment. 300,000 t of gypsum is also produced in the fertiliser industry. Following the registration, the collected data for the industrial activity were introduced and processed by a database installed in Windows. All the registered data were classified according to the industrial branch and sewage facilities. The marking of industrial units was done on maps by means of identification codes.

Table 7. Number of registered industrial units per branch and study area (Attika incl. Eleonas, Viotia)

Branch	Waste reduction	
	Without conversion of process technology	With conversion of process technology
Dye-finishing works	Use of biodegradable desizing and dyeing agents	Reduction of the volume of dyeing bath
	Two-stage bleaching with ClO- and H_2O_2 or CH_3COOH	Dyeing in an autoclave with CO_2
	Use of dyes with high fixing ratios and low heavy metals concentration	
	Recycling	
Tanneries	Use of chemicals which reduce the pollution load	Combination of several process stages in one bath
	Screening of organic residues	Cr recovery through sedimentation
Industry producing lead accumulators	Cooling water recycling	
	Reuse of cleaning waters	
Plating works	Increase of the number of rinsing steps	Physical metal recovery methods from depleted baths (only for big production units)
	Recycling of rinsing baths to the plating bath	
	Reduction of the bath concentration	
Industries with oil residues	Recycling of cooling water	
Basic metals	Cooling water circulation	
Production of fertilisers and acids	Recycling of cooling water	
	Reuse of wastewater streams	
Artificial silk industry		Spinning bath evaporation
		Recovery of CS_2 and other raw materials and reuse
Paint industries	Reuse of cleaning waters in the next batch of the same product	
	Closed circuits of cooling waters	
Production of insulation materials	Recycling of wastewater	
	Organisational measures for the reduction of rinsing waters	

Table 8. Summary of the measures for waste reduction at source

Industrial Branch	Number of units per study area	
	Attika	Viota
1. Dyeing-finishing works	131	12
2. Tanneries	15	4
3. Production of lead accumulators	26	1
4. Plating works	149	1
5. Industries with oil residues		
Used oil refineries	5	8
Oil refineries	2	–
Companies selling and distributing oil	9	–
Shipyards and ship repair works	2	–
6. Basic metal industries	441	56
7. Chemical industries		
Production of acids and fertilisers	1	2
Production of artificial silk	1	–
Production of paints	113	13
Production of insulating material	7	2

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