WORLD ENVIRONMENT CENTER

ENVIRONMENTAL AND WASTE MINIMIZATION ASSESSMENT

CHEMOPETROL FERTILIZER COMPLEX

LITVINOV, CZECH REPUBLIC

JUNE 20 - JUNE 30, 1994

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WASTE MINIMIZATION OPPORTUNITIES

at

CHEMOPETROL LITVINOV
AGRO DIVISION

LITVINOV, CZECH REPUBLIC

June 20-30, 1994

by

Bhaskar Bandyopadhyay

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I EXECUTIVE SUMMARY

Sponsored by the World Environment Center, New York, two Technical experts from the US visited Chemopetrol's facility at Litvinov, Czech Republic during June 20 through 30, 1994.

The purpose of the visit was to identify waste minimization opportunities at the production facilities of the AGRO Division of Chemopetrol and to recommend means of achieving those opportunities. Waste minimization and pollution prevention techniques such as examination of raw material consumption's and comparison against industry standards, opportunities of conversion of waste to useful product as well as conventional pollution abatement methods were used during the visit.

Discussions and plant visits were conducted at each of production facilities of the Agro Division which included several Air Separation Units, five Partial Oxidation Units, three Ammonia Synthesis Units, a Urea plant, a Carbon Black plant and a Catalyst production facility. Discussions and site visits were also conducted with the Environmental Protection and the Water and Waste Management Departments as well as the Research Institute of Chemopetrol.

Several waste minimization opportunities in AGRO Division were identified-some are near term and a few longer term. By far, the greatest opportunity in the short term is the resolution of the problems with soot water from the partial oxidation unit. Soot water is presently disposed in the sludge field along with fly ash and biological water treatment sludge. The annual volume is 8,000 tons and it is anticipated that there would be a large fee associated with its disposal and it may not even be allowed to be disposed of in that manner by 1998 or earlier. Yet, soot water is a valuable raw material for the production of carbon black, Chezacarb, that potentially has a multitude of use in domestic and world markets.

The design capacity of the carbon black plant is 5,000 tons per year. The production in the recent years has been limited to less than 1,000 tons per year due to the lack of demand. However, the Research Institute has recently developed new uses of the product and there is a strong possibility that the entire capacity of the plant can be sold or otherwise used in the very near future.

The upper management of Chemopetrol has just approved the use of carbon black for consolidation of sludge waste from oil waste lagoons, the present inventory of which is 160,000 cubic meters. This can tie up over 10,000 tons of carbon black or two years of production at the design rate. In addition, continued annual oil sludge production, estimated at 20,000 tons per year, will consume 2,500 tons of carbon black annually. The other uses identified by the Research Institute including use of the material to improve conductivity of rubber and clean up of oil spills and waste water clean up in automotive repair shops using portable units.

The carbon black plant presently can not be produced at the designed capacity. It can be corrected by debottlenecking the final product dryer by capital modification, estimated earlier, at 500,000 Kc. This estimate should be confirmed and the capital should be allocated for de-bottlenecking the plant. This will consume another 4,000 tons of soot carbon and reduce the soot disposal problem by a like amount. This will reduce the soot disposal fee by 20 million Kc or USD $715,000.

The next problem is ammonia and urea losses in urea plant. Ammonia usage in the urea plant translates to a 3,000 tons per year waste when compared to industry standard for such plants. We recommend employing an engineering consulting firm or forming an engineering team from within Chemopetrol to conduct a thorough material and energy balance around the urea plant to define the opportunities for ammonia usage reduction. The combined market value of the 3,000 tons of ammonia and the reduction in the potential fees associated with the discharge of ammonia in water amount to over 14 million Kc or USD $500,000 per year.

Ammonia losses and carbon dioxide emissions in the Partial Oxidation unit are rather high. Both should be investigated by employing an engineering team who should conduct a material and energy balance across the production unit. The CO_2 emission from the AGRO Division has been estimated at 600,000 tons per year, more than 10% of the total CO_2 emissions from Chemopetrol that includes the power generation plants and the other petrochemical plants. Although it is not considered a pollution problem, at least in the short range, there appears to be some opportunities for minimizing waste and reducing raw materials and hence cost.

Finally, the catalyst production facility generates small quantities of NO_x during one of the processing steps, However, the facility has already taken steps to install a system for NO_x abatement. The project should be completed.

The major hindrance to progress in the waste minimization and pollution prevention area appears to be the steep competition for capital for such purposes. It is estimated that 8 billion Kcs are needed for capital modification to meet the standards of the 1998 Environmental Regulations which is eight times the reported pre-tax profit of Chemopetrol in 1993. Furthermore, Energy and Petrochemical Divisions receives higher priority because of severity of problems and demands.

The Research Institute of Chemopetrol has made progress in contacting certain Western companies to promote use of the Carbon Black. Co-funding and profit sharing by such companies can ease the capital availability problems significantly and should be explored more thoroughly.

II INTRODUCTION

Dr. Bhaskar Bandyopadhyay, Technical Manager, Occidental Chemical Corporation and Mr. Wesley W. Atwood, a consultant and former Environmental Manager at Occidental Chemical Corporation visited Chemopetrol's facilities at Litvinov, Czech Republic during June 20-30, 1994.

The purpose of the visit was to identify waste minimization opportunities at the production facilities of the AGRO Division of Chemopetrol and to recommend means of achieving those opportunities. Waste minimization and pollution prevention techniques such as examination of raw material consumption's and comparison against industry standards, opportunities of conversion of waste to useful product as well as conventional pollution abatement methods were used during the visit.

The visit was organized by the World Environmental Center (WEC) under a cooperative agreement with the United States Agency for International Development (USAID) in Washington, DC.

Chemopetrol Litvinov has ranked among the key Czech enterprises owing to its size and the diversity of production which makes it the largest refinery-petrochemical complex in the Czech Republic. It is the largest producer of motor fuel or gasoline and heating oil and is an important supplier raw materials to other chemical and processing industries.

In 1993, Chemopetrol was reorganized following cessation of state control and establishment of a joint stock company on January 1, 1994. Presently, the company consists of 10 divisions, 6 production and 4 service oriented, and two business units. The 6 production divisions include the Refinery Division, the Petrochemical Division, the Phenols Division, the Energy Division, the Agro Division and the Water and Wastes Division.

In 1993, Chemopetrol invested 1,865.9 million Kc on 133 capital projects of which 1,627.2 million Kc was spent on 77 projects major projects requiring 10 million Kc or higher. A substantial portion of this capital , 604.5 million Kc, was spent on some 44 environmental projects. Most involved solutions to problems with gaseous and solid emissions from local heating plants and emissions of light hydrocarbons from refinery and petrochemical production units.

III WASTE MINIMIZATION TECHNIQUES

Many techniques have been successfully used in the chemical industry to reduce pollution. However, the most rewarding are those which reduces the waste generation thus saving not only waste abatement cost but frequently reducing raw material wastes. The following basic techniques of waste minimization and pollution prevention apply to the Agro Division plants and process.

Raw Materials Quality Improvement

Process should be operated with raw materials of consistent and desirable quality which maximize yield of the desired product and minimize the formation of wastes. The partial Oxidation Units of the Agro Division uses heavy crude bottoms quality of which may vary giving rise to excessive soot carbon as well as carbon dioxide productions. Establishing consistent quality crude and hence the crude bottoms may pay dividend in this process.

Raw Material And Energy Yield Improvement

It is believed that techniques involving raw material and energy yield improvements are the most cost effective means for waste minimization. Process yields can be improved by a number of ways.

Process optimization or optimization of process operating condition such as temperature, pressure, concentration, residence time, etc. is most easily implemented as it does not require any significant expenditure of the capital. Frequently, those close to the operation can optimize the process given the right tools, such as on-line analyzers or appropriate measuring devices.

Continuous Process Improvement is also a powerful tool for improving process yields. It involves identification of the process characteristics, measurement of those characteristics and control charting the same. Process has normal variation and abnormal variation which is identified by the control charts. Operators investigate all abnormal variations. Operators must find the reasons for the abnormal variation and eliminate the causes for abnormal variations which are detrimental to the process and incorporate those causes or process conditions which result in an improvement to the process.

Process Modification is another way to improve process yields. It may involve only minor modification such as changes in process flows or reaction sequences in multistage processes or may require extensive additions and revisions to the process system. A good example is the ammonia production facilities in the Agro Division. There are three synthesis units in the plant capable of operating as independent trains. However, these units are operated in series to maximize conversion of hydrogen and nitrogen, the raw materials.

Material and Energy Balance of the process is a key step for determining which of the above methods should be used especially where large amounts of waste are identified or suspected. Thorough balance should tell the source of the waste and even suggest immediate corrective actions which may be implemented without further study. It also should suggest which of the method should be tried to minimize waste production. In Agro Division, both the Partial Oxidation plants and the Urea plant are excellent candidate for conducting such material and energy balance.

New Technology And New Product

New technology is required when existing technology fails to yield the desired result. New technology may involve replacement of the existing plant processes and construction of new plants or development of processes for consuming waste and development of market for the by-product. Agro Division has example of both. The old Air separation plants are gradually phased out and replaced with new plants of much higher capacities. They produce much less wastes. The soot water waste produce in the Partial Oxidation Units are converted to Carbon Black. Research Institute has found new uses of this carbon black and found ways to manipulate the properties of the product. Called Chezacarb, the product should have world wide market.

Recycle and Recovery

Recycle of waste stream and recovery of product losses can be frequently implemented with financial benefits. It may involve installation of equipment to capture product losses or conversion of waste so that it can be recycled to the front end of the process. Recapture of product losses from the.urea prilling tower using a bag house of similar devices is a good example of this technique for waste minimization.

Detoxification of Wastes

When all techniques for waste minimization fails, detoxification of waste should be evaluated as the remaining alternative. Stabilization with lime and cement is a common technique for stabilizing waste. Chemopetrol plans to utilize this method to stabilize calcium sulfite slurry waste from the flue gas desulfurization process. This process is being installed in one of the high sulfur coal burning power plants. A second example is the use of carbon black for stabilizing waste oil field sludge. The project has been recently approved by the Chemopetrol management.

IV FINDINGS

The production facilities of the Agro Division include several Air Separation Units, five Partial Oxidation Units, three Ammonia Synthesis Units, a Urea plant, a Carbon Black plant and a Catalyst production facility. In addition to conducting visits and discussions with plant production personnel, discussions and site visits were also conducted with the Environmental Protection and the Water and Waste Management Departments as well as the Research Institute of Chemopetrol.

Production Facilities

The following is a summary of the production units including the plant design capacity and present utilization rate.

Unit	Capacity	Year built or Modified	1990 Production	% Utilization
Air Separation	315 MM m^3 O_2	1942-1975	282 MM m^3 O_2	90%
	470 MM m^3 H_2		381 MM m^3 H_2	81%
Partial Oxidation	1,000 MM m^3 H_2	1972	880 MM m^3 H_2	88 %
Ammonia	350,000 tons	1955-1977	329,521 tons	94 %
Urea	200,000 tons	1972-1984	197,070 tons	99 %
Carbon Black	5,000 tons	1985	846 tons	17 %
Carbon dioxide	80,000 tons	1965	9,065 tons	74 %

Oxygen Production (Air Separation Units)

Oxygen production represents one of the oldest technology. The first building (the building we were in) was constructed during the German occupation. It was a part unit for production of gasoline from lignite. The plant in this building was expanded in stages until 1955 using the old technology. The production in this building has been limited; some production units have been dismantled.

Air under high pressure (200 bars) is cooled using ammonia refrigeration system. Before compression, the CO_2 is removed by scrubbing air with caustic soda. It is a high energy consuming process and is not considered economic. The oxygen is separated from nitrogen by a cryogenic distillation process.

In the new building, the high pressure technology is not used. The air is not scrubbed with NaOH and it does not need NH_3 refrigerant. Four units were constructed during 1956-1973. Compressors were used for compressing air as well as O_2 and N_2. Nitrogen is compressed to 320 bars and is used in the production of ammonia.

In the third building, units with much higher capacity are to be installed for the production of oxygen and nitrogen. The capacity of this unit is equivalent to the capacity of 4 units in building 2. Air at low pressure (4.8 bars) is cooled down to -174 to -195 ^{o}C. This is the largest production unit for oxygen. The compressors are located in five other buildings.

The oxygen is 97% pure, remainder being mostly nitrogen and nitrogen is very pure with only less than 100 ppm oxygen in it. Oxygen with 99.5% purity is sold as bottled gas.

One problem noted in this processing units is the noise, Noise is produced during the switching over of the cycle of the air separation. Noisy environment requires ear protection and the discipline to make people use them which is not enforced. Audio metric testing, both baseline and periodic, are conducted.

Used oils from compressors are consolidated in one place. It is filtered or centrifuged to separate the solid waste. The solid waste is sent to Ostramo plant in north Moravia for regeneration of oil.

The spent scrubber water (containing sodium carbonate) from the old plant is diluted with water from other air separation plants and sent to water treatment plant. However, this is not expected to last as the old plants are likely to be shut down in three years.

POX (partial Oxidation) units

The POX units were built between 1969 - '71 and were tested in 1971-'72. Crude oil, atmospheric or vacuum distillation residues are partially oxidized to hydrogen and carbon monoxide using Shell technology. The CO is further oxidized to CO_2 by the shift gas reaction process.

Chemopetrol has six hydrogen generation units; five are operating units and the sixth idled unit is used for spare parts.

The reaction is carried out at 1350-1400 ^{O}C and 35 atm pressure. The proportion of oxygen to steam is 1.5. The product from the reaction has the following typical composition:

CO - 45%, H_2 - 45%, CO_2 - 4.5%, CH_4 - 0.3%, H_2S - 0.7%, COS - 0.1-0.2%, traces of HCN, NH_3 and N_2.

The ammonia that is approximately 80 - 90 kg NH_3 per hour, is removed by scrubbing with water. The soot (carbon) formation is between 1.5 to 2.5% by weight on the feed stock. The feed stock is all liquid. The reactor gases go to a waste heat boiler where they are cooled to about 250-300 ^{O}C. Steam pressure is 41 atm and temperature is 253 ^{O}C. Steam is used as various power sources as well as for dilution of oxygen fed to the POX unit. Gases leaving the boiler is quenched and washed with water to remove carbon soot. The HCN is scrubbed with cool water and the scrubber effluent is combined with the soot water and transported for disposal in the sludge field. The carbon in the soot water (14 g/l @ 20 cu. m./hr) reacts with HCN in the following manner:

$$HCN + H2S \text{ ----> } CNS'$$

The ratio of soot water to HCN water is 60:40.

The POX units generate two aqueous wastes: soot water and ammonia water.

Gas Cleaning Technology

After removing H_2S from the gas, it is reacted with steam over iron oxide-chromium oxide catalyst at a temperature of 300 ^{O}C to convert CO to CO_2 in a two stage reaction process. The steam to gas volumetric ratio is 1:1. The basic reaction is:

$$CO + H_20 \text{------> } CO_2 + H_2$$

In the first stage, the CO content drops from 47% to 8%. The temperature increases to 500 ^{O}C. The gases are cooled to 360 ^{O}C and passed over the same catalyst where the CO decreases to 4%. The final product contains 32% CO_2, 4% CO, 2% inert (N_2, Ar, CH_4), the remainder being hydrogen. There is a small amount of H_2S (50 ppm) as well.

The CO_2 is separated from hydrogen by absorbing with a 35% ethanol amine solution. After scrubbing the CO_2 drops to 0.1%. However, CO remains at around 5.5%. The CO is reduced by a low temperature (190 °C) conversion process using a copper based catalyst. After this conversion process, CO drops to 0.4%.

Ethanol Amine: (C2H5)2-N-COOH

COS is hydrolyzed using a catalyst at 200 °C in the following reaction:

$$H_2O + COS \text{ ----> } H_2S + CO_2$$

Carbon Black Production Unit

During partial oxidation of heavy residue, soot water is formed which is sent to the carbon black production unit. Originally, Phillips Petroleum was to supply a process for making a dry product from the soot for use in the electrochemical industry. All business arrangements were also completed. However, these arrangements fell through. Later, the Research institute developed the process to recover the soot as a new dry product. This is called carbon black or Chezacarb. The product is sold to Degussa who distributes it world wide.

The world's consumption of carbon black is 2,000 tons per year in the electrochemical industry. The carbon black is used in the rubber industry as anti static or conductive agent. The capacity of the Chemopetrol plant is much higher than the present market.

The incoming soot water is cooled from 100 to 40 °C and is then sent to the extraction equipment. The carbon is extracted from the soot water by contacting with light boiling (60-80 °C) fraction, "benzene" (gasoline). The soot and organic layer float up and are removed for drying. The drying takes place in two stages by contacting with live steam. Most of the gasoline is removed in the first stage and a mixture of carbon, gasoline and water goes to the second stage where it is contacted with a stream of steam and nitrogen mixture. The dried carbon at 200 °C is cooled to 50 °C in a fluid bed cooler using nitrogen gas. The cooled product is pneumatically transported to storage bins. Production, transportation and storage of the material are done in a nitrogen atmosphere.

The design rate of the unit is 5,000 tons per year of carbon black. However, the final product dryer capacity must be increased to achieve this designed rate. The capital cost is estimated at 500,000 Kc. A plant test must be conducted to verify the capacity of the final product dryer.

The product is shipped in large bags (1,700 liters) as well as standard (42 liters) bags. The product has a bulk density of 130 kg/cu.m. The specific surface area is 800-1000 sq. m./gm. A total of 16 parameters including particle size distribution, sp. gr., BET absorption isotherm and pH ([illegible] spirit) is measured.

Light fraction usage is as follows:

Total usage	3.5 kg/ 1.0 kg of carbon black
Fresh usage	30 gm/1.0 kg of carbon black

The concentration of soot in soot water 13-15 kg/cu. m.

Ammonia Synthesis Unit

The ammonia is produced by the classical high pressure process. The raw materials are hydrogen and nitrogen both of which are produced by Chemopetrol. The gases at 320 atm are introduced into the synthesizer that operates at between 25 and 30 MPa (250 - 300 atm.) and at 420-520 ^{O}C. An iron base catalyst is used. The capacity of the unit is 1,000 tons/day but is limited by the raw material availability.

There are three synthesizer units. Although each can operate as independent train, three units are operated in series to maximize conversion of raw materials to products. Argon and methane impurities in the incoming gases build up and slow the reaction down and hence operating the units in series is important.

The raw material consumption's are as follows:

Per ton of ammonia,

Hydrogen	2,100 cu.m.
Nitrogen	690 cu.m.

The gases leaving the stage III are scrubbed with water to remove ammonia. The 25 to 27% NH_4OH solution is in part used by the refinery division for treatment of acidity and in part sold to others for inorganic synthesis. Should the ammonia absorption system be unavailable the ammonia can be diverted to a flaring stack.

Storage:

10 underground tank	100 cu. m. @ 15 atm
11 above ground tanks	200 cu. m. @ 15 atm

Urea Production

The urea reaction proceeds through two stages: ammonium carbamate is produced in the first stage and urea in the second stage. Chemopetrol employs a Stamicarbon total recycle process; all gas from the low pressure section is recycled to the high pressure section. The reaction of ammonia and hydrogen is carried out at 140 atm. pressure and at 180 ^{O}C.

Urea dust loss from the priller is 180 to 320 tons/year

The raw material usage's are as follows:

CO_2: 430 cu. meter/ton
NH_3: 595 kg/ton

The NH_3 usage in typical plant is 580 kg/ton. The AGRO plant usage represents 3,000 tons/yr. of additional usage.

The plant reports all ammonia returned to the biological water treatment plant. Sampling is done every hour. The limit is 60 kg/hr $N(NH_4^+)$. On a 8000 hr/year basis, this represents a maximum loss in aqueous waste of 582 tons.
Projects to reduce ammonia usage and reduce wastes include:

- High pressure ammonia absorber
- Scrubber for Urea priller
- Retention Tank
- Hydrolyzer

Liquid CO_2 and Dry Ice Production Units

Present production rate 75,000 tons/year. The plant is being expanded to 130,000 tons/year at a cost of 300,000 Kc.

CO_2 from the gas cleaning section still contains some H_2S and NH_4 which must be removed for the production of food grade CO_2. H_2S is removed first by contacting with activated carbon (not carbon black). The spent carbon is returned to the supplier for regeneration or disposal. NH_3 is removed by scrubbing with water.

Catalyst Production Facility

Many of the catalysts consumed at Chemopetrol are produced in the facility. The process begins with coprecipitation of substrates, filtering the solids using a Russian design multi pass belt type filter with a large area followed by drying in ovens. The dry powdered substrate is then pelletized in pelletizer and dried. The catalyst is impregnated on the dried pellets and is further dried/calcined, as required to produce the desired catalyst. They do not reprocess used catalyst.

Environmental Aspects:

General Description

The environmental matters related to Agro Division and across the Chemopetrol complex are as follows. Due to the integration of the waste handling of the Division with the total complex, review of both is pertinent.

Environmental protection is important not only for the protection of the environment, there is economic incentive as well. There is a direct incentive for reducing waste as there are stiff fees associated with disposal waste and especially hazardous waste. Environmental laws passed in Czech Republic in 1991 has rapidly escalating fees with time.

Governmental agency (Administration for the River Basin) sets the water quality limit. The water use at the Chemopetrol facility constitutes ninety percent of the water flow in the river Bilina. Water is used for a variety of purposes including transportation of solid waste to land fills. The water treatment receives considerable attention that includes biological treatment of waste water. Any problem with water quality must be reported to the Administration for the River Basin.

A hydrological study has just been finished. On the basis of the results, monitoring wells have been installed at critical locations. Not only river Bilina is involved, there are several small brooks associated with the water system.

The ground water is polluted from many years of seepage from the Chemopetrol operation. Surface water can get contaminated from rising level of ground water that can leach additional pollutant to the surface water. This is a concern. Presently the ground water (not surface water) is pumped out for underground mining operation and this water is released to river Bilina, after appropriate treatment.

On air, there is a concern for SO_2 and NOx. Chemopetrol burns high sulfur coal. However, this concern should be eliminated shortly as the plans - to install a flue gas desulfurization process, which is already under construction, and to shut the two other power plants by 1998 - are implemented.

The power plant stack gases will be scrubbed with $Ca(OH)_2$ slurry and that will nearly eliminate SO_2 emissions. The NO_x will also be reduced substantially by appropriate boiler modification. The solid waste from this operation, a slurry of $CaCO_3$ and $CaSO_3$ together with fly ash, will be used to stabilize sloped sides from coal mining operation, Largest waste is ash and slag from the power plants. This waste is hydro-transported to a sludge field (an area leased from a strip mining operator). The life of this land fill is to year 2025. Soot (7,000t tons per year) from the Agro division is sent to the same sludge field under a special arrangement with the authorities that runs out in 1996. Soot water is considered dangerous and high fees are paid for its disposal. The environmental problem with soot is the heavy metal contents (e.g., vanadium). There is a danger that soot disposal in this site will be prohibited in the future.

The new dump site, owned by Centro-Odpady, a separate share-holding company, will be located in the city of Most. It will be good for 20 years. Chemopetrol will own a number of shares of the company as well. Hazardous waste (phenol contaminated $CaCO_3$--10,000 tons per year) will go to this land fill. Presently this waste is disposed in a separate land fill which will expire this year.

The last is the liquid waste- tars and liquid wastes from processing units. This type of waste is stored in so called oil lagoons that were built on sites where Winkler generator waste had been stored. The Winkler generator waste was covered with a clay lining before storing the oil waste. Over the past 40 years, a total of nearly 180,000 cu meter of liquid wastes has been so stored in various sites. Water separated from the oil lagoon contaminated with phenol is treated in the water treatment plant.

Much remediation of the oil sludge land fills was initiated in the last two years. Martech, a US. Company, did a survey to asses the quality and quantity of liquid waste. On the basis of the finding, an Italian company developed the treatment process. It is based on separating the water, oil and the solid components. The solid components are to be further solidified with CaO and then disposed of in the land fills. Water component will go to the water treatment facility. The oil phase will be returned to the refinery.

Incineration plant is used to burn mostly organic combustible matters. There is no treatment of the stack gases. The new air pollution regulation must be met by the incineration plant by 1997 as the present permit will expire.

Water and Waste Division

Water and waste water Division is responsible for both solid and water waste management.

The old landfill is almost full. A new landfill will be opened. Centro-Odpady, a new company, will be manage this landfill. It will be used to store for all solid waste that is around 70-80 thousand tons per year.

The solid wastes include approximately 10,000 tons of limestone contaminated with phenol and 500,000 to 700,000 cu. meters per year (60-70,000 tons per year) of fly ash from power station. Solid wastes are transported by specially lined pipelines to the sludge field and the decanted water is pumped back. Some water from this field is discharged to Bilina.

Some 8,000 cubic meters of oil/water residue from various plants is stored around the plant property at several locations. All water from the refinery is contaminated with oil and the water must be treated. A two stage centrifugal separation system is in the process of being installed. This will separate the solid waste from the oil/water mixture first, then separate oil from water waste. Research has shown that the solid waste can be mixed with carbon black at a weight ratio of 7-8 waste 1 and then burned in the power stations.

Waste Water Treatment Plants

Oil based matters are separated by mechanical means in the chemical plants before sending to the water treatment facility. Sulfide is also removed from the waste water at the chemical plants utilizing catalytic oxidation with air.

Chemopetrol discharges 31 million cubic meter per year or nearly 22 MGD of waste water. The biological treatment handles only 8.8 million cubic meters per year and the remaining water is mechanically treated.

Water is treated in stages; first a secondary treatment for oil and then to biological treatment. After treatment, the following limits are met: 8-10 ppm BOD and 5-10 ppm $N(NH_4)$.

Rain fall (estimated at 450 mm/yr.) collected in the plant sewer system, cooling tower blow down, sanitary wastes from the plant as well as sanitary waste from the city of Litvinov go to a mechanical cleaning station for treatment and release to river Bilina. The quantity of this water is approximately 2,500 cu. m./hour.

Fee for discharging $N(NH_4)$ is approximately 9 MM Kc/yr. for discharging approximately 975 tons/yr. of nitrogen. AGRO division discharges approximately 659 tons and rain water contributes another 240 tons. The total fee to be paid in 1994 is estimated at 18 million Kc's. It is based on BOD. Fees for $N(NH_4+)$ are expected and are estimated at 9 MM Kc/yr. with 80% attributable to the AGRO Division. Fees for heavy metals are also expected to be in place in 1995 but the Waste & Water Division sees no problem meeting the 1995 standards.

The City of Litvinov pays fees and cost of service to treat their municipal waste.

Environmental Issues

Although the end of the pipe line samples of waste proved to be a non-hazardous waste by leaching tests, Czech environmental agency still considers the wastes hazardous. Chemopetrol has some open questions on fees assessed in 1992 and 1993 due to differences in interpretation of the regulations. Now it is in court. The agency has imposed rate II fees for 1992-1994 because of the lack of lining in the sludge field.

After 1998, Chemopetrol will produce no fly ash, soot water, biological water treatment plant sludge or water from crude oil desalting operation.

Economic Factors in Environmental Matters

Agro division's sale represents 8-10 % of the total sales for Chemopetrol. Allocation of capital by Chemopetrol is not proportional to this figure. Refinery Division receives the highest priority after the Power or Energy Division.

The Research Institute's Role

This is the only industrial research facility in Czech Republic. The institute serves a market larger than Chemopetrol. It plays four major roles:

1. Assist in diversification of crude oil supply. The challenge is to secure oil other than Russian crude.

2. Maintain the product at competitive level. [Several years ago, there were practically no competition.] Competitive means low cost and environmentally friendly products.

3. Develop tailor made processes to utilize by-products, wastes and for better utilization of crude oil.

4. Engage in environmental protection issues. Environmental protection is becoming more important for the company, the chemical industry and the Research Institute's research thrusts.

The institute has 180 employees and has an annual spending of 60 million Kc. The institute has 36 contract research today.

Environmental protection has 3 aspects.

- To keep technology at acceptable levels.
- To keep products acceptable
- Waste conversion

CARBON BLACK- CHEZACARB

Carbon black, called Chezacarb, has unique physical properties and the material should not be wasted by burning as a fuel. Carbon molecules orient themselves in one plane. Particle size of soot is between 1 and 10 nano-meters. This property makes it suitable as a conductive material. Because of this, it can be injected into plastics to improve electrical conductivity, good for transporting gasoline.

Chezacarb also has very high specific surface area, 800- 1,000 m^2/gm., better than active carbon. It has pore structures with pore size between 1 to 1/1000 nanometer and it can be controlled. The specific pore volume is between 3.5-4.5 cc/gm.

The product is sold in the West under the name -- Printex-XE2, which is used to improve electrical conductivity of plastics.

The plant capacity to produce Chezacarb is not fully used today and soot water is disposed off in the sludge field. It is hoped that this is the last year that the soot is disposed off in such a manner. Next year, only 15-20% of the capacity will be used for improving electrical conductivity properties and the rest will be used for ecological benefit as sorbent.

Chezacarb, in spherical shape, is not the best form for use as adsorbent because of high pressure drop across the adsorber bed and because of difficulty in regenerating such beds. Research Institute has developed ways to produce the material in different shape -- 2-10 mm extruded pellets. It can also be produced in the shape of normal active carbon.

Chezacarb is a good adsorbent for crude oil, especially useful in cleaning up accidental releases. One kg of Chezacarb can adsorb 6 liters of crude oil. Czech Army uses the material for such purposes. Chezacarb has one not so good property the black color. Even it is one of the best sorbents, the black color is unappealing to users.

Socks containing Chezacarb can be used around leaky equipment. Connected bags of carbon black are good for floating in water and containment of oil.

Chezacarb can work as a catalyst for HCN and H_2S abatement. Research Institute has developed equipment based on Chezacarb for treatment of waste water and recently furnished such equipment for France and Switzerland. This is particularly suitable for purifying and recycling of waste water from automotive maintenance shops. Textile factories represent another application.

Vanadium in carbon black is 0.4-0.8% depending on the feed stock. It can be lowered to 0.12%, but what can be done with the vanadium that is removed from the soot. Top management must allocate funds for this project as expanded use of Chezacarb can result in to hundreds and thousands of Crone savings.

Research Institute has developed pelletized fuel from carbon black and oil sludge mix. Agro management is optimistic about the prospect of such a possibility.

Conventional solidification of oil sludge is done with clay/lime mixtures. The process requires 9 tons of clay/lime per ton of organic sludge. Further, the product is not free from hazards leaching of constituents such as phenol. By contrast, 1 part of carbon black can consolidate 7-9 parts of wastes. Much work has been done by Mr. Nacesani, Head of the Pilot Plant. Market survey has also been conducted. Technical negotiations with potential partners are also underway.

Nine grades of carbon black products are offered. Market in Czech Republic is open to the products. Application is promising in pollution abatement in three areas:

- Purification of semi-solids
- Purification of liquids
- Purification of gases

Estimated markets:
Crude oil spillage control -- 400 tons/yr.
Conductive agent for rubber -- 600 tons/yr.
Oil sludge consolidation -- 20,000 tons sludge generated annually which may
consume 2,500 tons/yr.

V CONCLUSIONS & RECOMMENDATIONS

The Agro Division of Chemopetrol Litvinov has a several opportunities for waste minimization which should not only reduce waste but will improve profitability. In order of priority with no cost and low cost solution these are as follows:

Soot Water from Partial Oxidation Units: An estimated 8,000 tons per year of carbon suspended in water is produced in the Partial Oxidation plants. Although a Carbon Black plant can convert 5,000 tons to a useful product, less than 1,000 tons are so used. The remainder is discharged to a sludge field. The soot water has been classified hazardous by Czech Environmental Regulators. The disposal fee in 1994 for hazardous waste of this nature is set at 4,000 Kc per ton. Further, It may not be allowed to dispose of in that manner in the near future,

The Research Institute has developed a multitude of new uses of the carbon black product, called Chezacarb, which should have both international and domestic demand. The new uses shoould permit the plant to operate at capacity. The plant has a bottleneck, which is capacity constraint of the final product dryer, and can be removed with a capital investment of 500,000 Kc. It is highly recommended that the carbon black plant be de-bottlenecked in an expeditious fashion.

Ammonia losses from Agro Division's plants is estimated at nearly 4,900 tons per year. Much of this losses occur in the Urea plant. The ammonia usage in the Urea plant is 595 kg/ton. When compared with typical plant usage of 480 kg/ton, the Urea facility must be loosing 3,000 tons per year of ammonia above a typical plant. A thorough energy and material balance must be conducted to determine the source or sources of the ammonia losses and to determine corrective actions. Strong considerations should be given on employing a consulting firm, such as Chemplant Technology, who has been retained by Chemopetrol on other projects for the last 10 years, to conduct the study.

Urea product losses from the prilling tower have been reported at 180 to over 300 tons per year. The material balance study, suggested above, should also confirm the true losses and provide justification for installing a suitable dust collection equipment.

Carbon dioxide emission from Agro Division has been estimated at 600,000 tons per year. The likely source is the Partial Oxidation Units. It is highly recommended that a thorough energy and material balance be conducted around each of the units to investigate corrective actions neceesary. There is an economic incentive for reducing this waste as losses of carbon dioxide is really the loss of raw material. Here also, strong considerations should be given on employing a consulting firm for the project.

VII COST AND PAYBACK ESTIMATES

Utilization of carbon - An Alternate to Soot Water Disposal

According to Czech Environmental laws, the soot water is considered a hazardous waste. The 1994 charge or feed for depositing such hazardous waste in waste dumps is 5,000 Kc/dry ton. Presently, 7,000 tons of the carbon in the soot water is disposed of in the sludge field. The disposal fee is therefore 35,000,000 Kc or nearly USD $1,250,000 per year.

In addition to reducing cost, an additional 1,000 tons per year of the product Chezacarb, may be sold at a price equivalent to active carbon or over 70 Kc or USD $2.5 per pound. This would generate an additional 15.4 million Kc or USD $550,000 per year.

The carbon black, which presently consume nearly 1,000 tons of soot, can be debottlenecked to consume an additional 4,000 tons of dry matters in the soot water reducing the disposal fee by 20,000,000 Kc or about USD $715,000 per year. The final product dryer which serves two carbon black production train must be upgraded or a parallel unit must be installed for the plant to produce at the designed capacity.

The total potenital benefit is 35.4 million Kc or USD $1,265,000 per year.

The capital requirement was estimated by Agro Division at 500,000 Kc or about USD $18,000. This estimate is soft and must be firmed up. However, even if the capital is increased 10 folds to 5 million Kc or USD $180,000, the project still has a very short pay back time.

Reduce Ammonia Losses in Urea Plant

The ammonia losses in the urea plant is estimated at 3,000 tons per year. According to the Waste Water plant management, the fee for the disposal of approximately 975 tons per year of ammoniacal nitrogen, $N(NH_4+)$, of which 80% is attributable to Agro Division, is 9,000,000 Kc or USD $320,000 per year. Both the Urea plant and the Partial Oxidation Units contribute to the ammonia in waste water. The market value of the ammonia being lost is over 8.4 million Kc or USD $300,000 per year. Thus, the total potential saving is over 14 million Kc or USD $500,000 per year.

Two projects have been identified by Agro Division to reduce ammonia and urea levels in the waste water. These are: 1) Construct retention tank at cost of 9,500,000 Kc or USD $340,000 and 2) Urea hydrolysis unit at a cost of 16,500,000 Kc or USD $590,000. Thus the total capital is around 26 million Kc or $930,000.

We believe that a thorough material and energy balance around the plant may result into finding a more cost effective solution to the excessive ammonia usage problem. This may also lead to a significant reduction in the ammonia in the waste water thus provide the maximum benefit with a 2 to 3 year payback.

Reduce Urea Product Losses

The product losses in the prilling tower is estimated at between 180 to 300 tons per year. At the present market value, the product loss is equivalent to between 1.26 million to 2.1 million Kc or USD $45,000 to $75,000 per year. Strong consideration should be given on installing a suitable product recovery equipment which may include a scrubber and scrubbing solution recycle and recovery system. The system cost should not exceed 14 million Kc or USD $500,000. Thus, in this case the pay back is 7 to 8 years.

Reduce Carbon Dioxide Emission

Presently there is no penalty of fee associated with the estimated 600,000 tons per year carbon dioxide emission from the Agro Division's plants. It is suspected that much of the waste originates in the Partial Oxidation units from poor yield from the crude bottoms. The amount of crude bottom equivalent to the carbon dioxide is nearly 200,000 tons.

The energy equivalent value of the crude losses, at 12,000 Btu per pound of the crude bottoms and 70 Kc /MM Btu or USD $2.5/MM Btu, is 33.6 million Kc or USD $1,200,000 per year.

The above figures are estimated without a great deal of hard data. However, the magnitude of potential for saving is certainly large enough to justify the cost of resources to conduct a thorough material and energy balance around the POX production units which should lead to confirmation or revision of the losses and to one or more potential solution. The cost of such a study is estimated to be 4 man-months or 1.4 million Kc (USD $50,000) including labor and materials.

VII APPENDICES

APPENDIX A

SAFETY BRIEFING

Standard safety rules applicable to chemical industry applies here also.

No smoking anywhere in the plant.

No flash photography as some can cause ignition of combustible vapors.

No alcohol.

Cameras, computers etc. must be declared at the receptionist's desk due to security matters.

Always have a Chemopetrol escort when visiting any part of the plant.

Watch for traffic, many RR crossing, many vehicles.

Report any incident/accident while in the property.

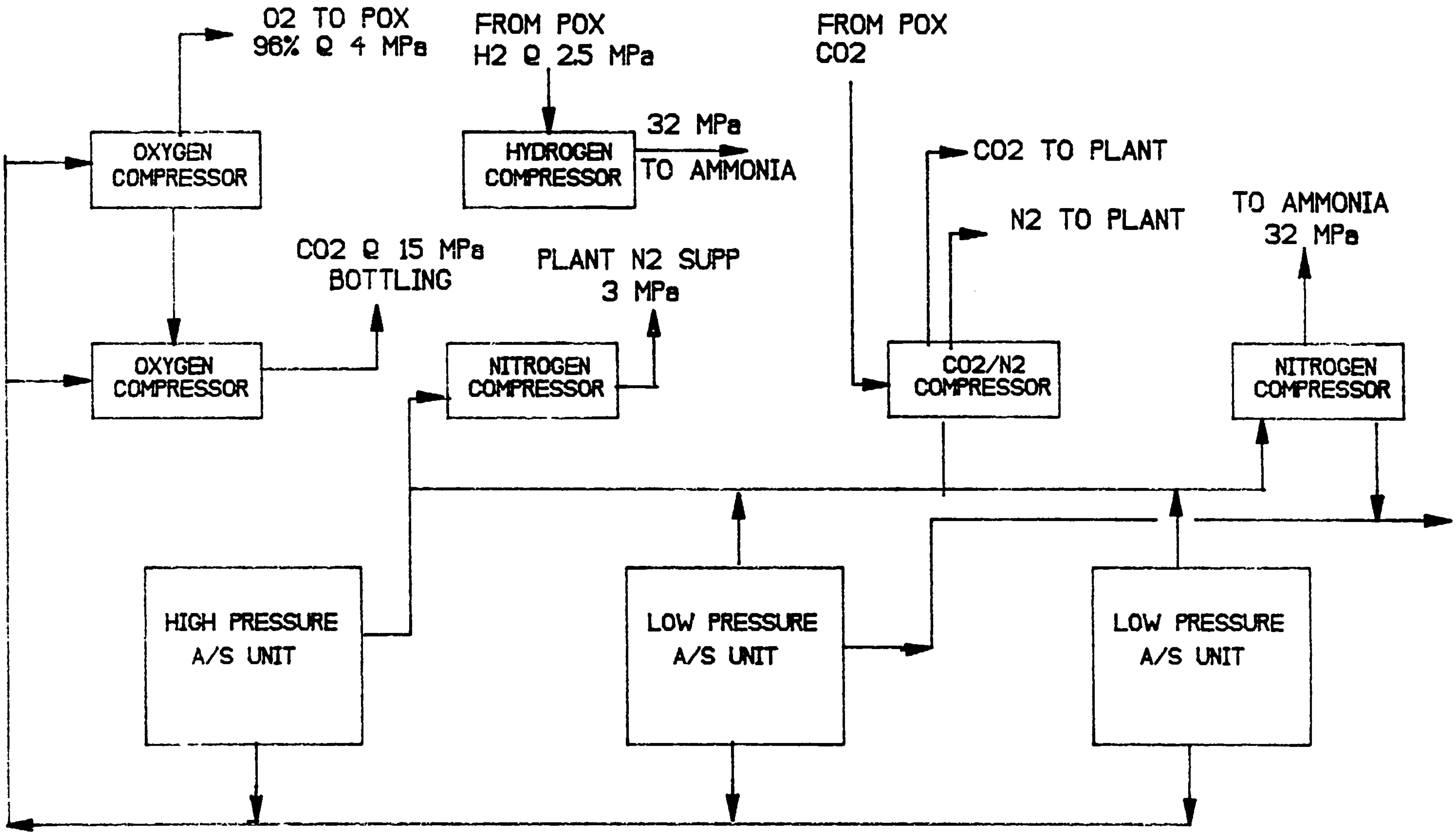
Watch out for any falling objects from the many pipe bridges within the plant

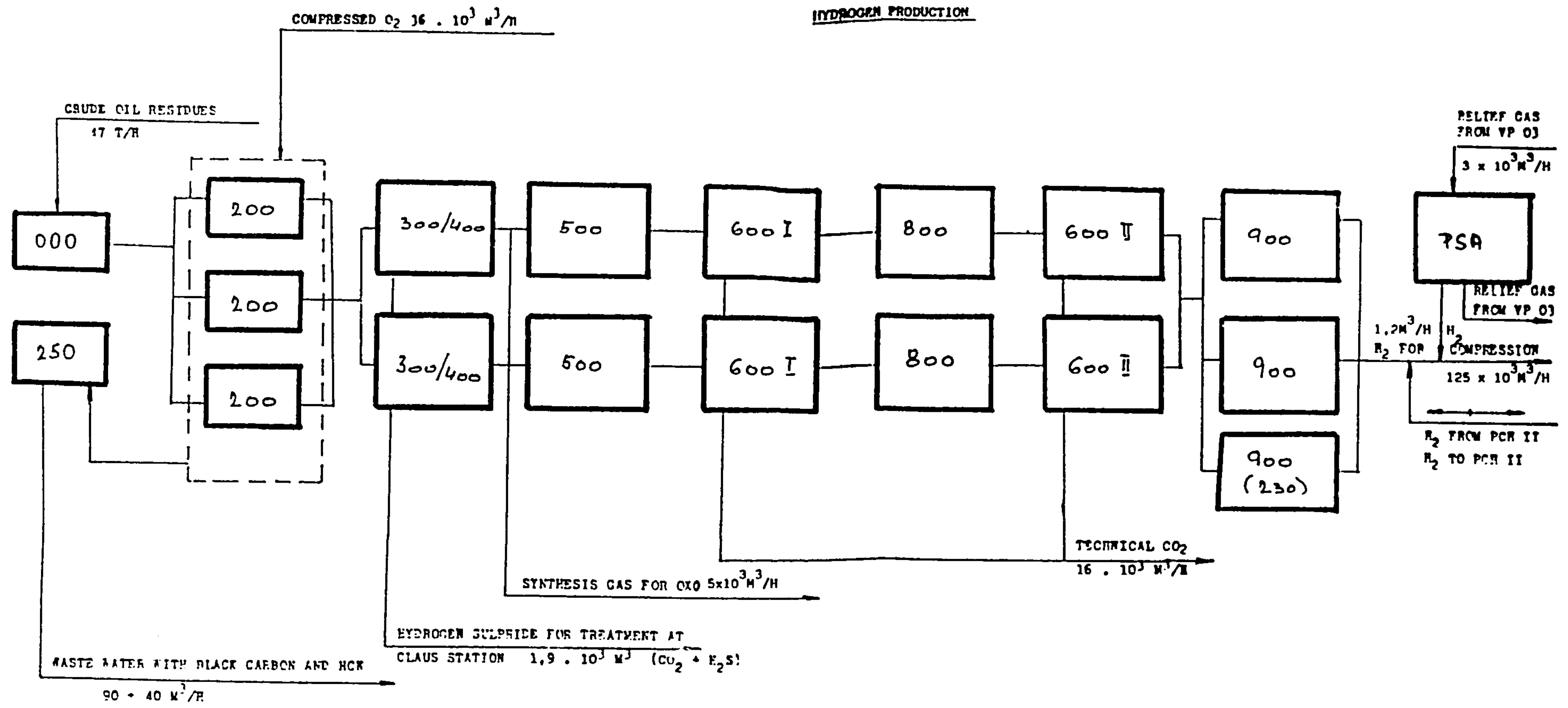
APPENDIX B

This section contains the following flow sheets and schematic diagrams:

- Air Separation Unit Flow Sheet
- Partial Oxidation (POX) Process Flow Sheet
- Carbon Black Process Flow-Sheet
- Ammonia Process Flow Sheet
- Ammonia Synthesis Units & Ammonia Abatement Schematic
- Urea Process Flow Sheet
- Liquid CO_2 & Dry Ice Process Flow Sheet
- Water Treatment & Discharge to River Bilina Schematic

AIR SEPARATION AND GAS COMPRESSION





000
STORAGE RAW TANK

250
SEWAGE WATER
TREATMENT AND
PELLETIZING -
- PETCRICITION
BY AIR/REMOVAL
CARBON BLACK

200
GASIFICATION SHELL
PARTIAL OXIDATION
BY O_2 + STEAM

300/400
ALKACIDE - WASHING
AND COS - HYDRO-
LYSIS
DESULPHURIZATION
OF GAS AND COS
HYDROLYSIS ON
CATALYST

500
HIGH - TEMPERATURE
CONVERSION
CONVERSION BY
STEAM ON CATALYST

600 I
CO_2 WASHING
I. STAGE
WASHING TEA

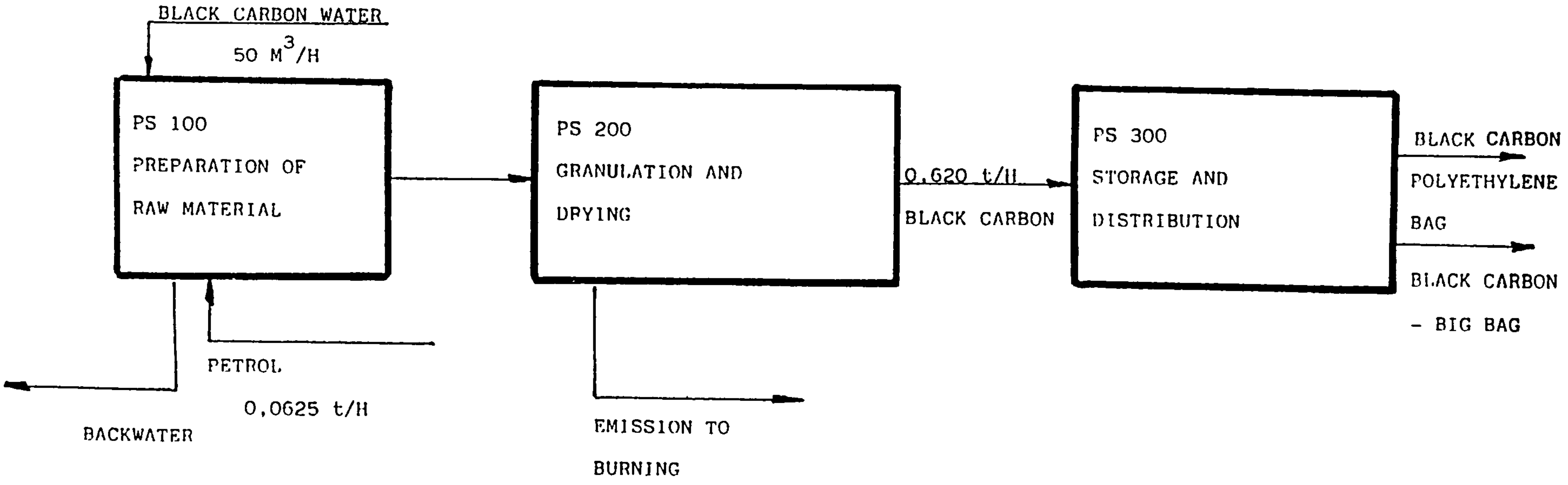
800
LOW-TEMPERATURE
CONVERSION
CONVERSION CO
BY STEAM ON
CATALYST

600 II
CO_2 WASHING
II. STAGE
WASHING TEA

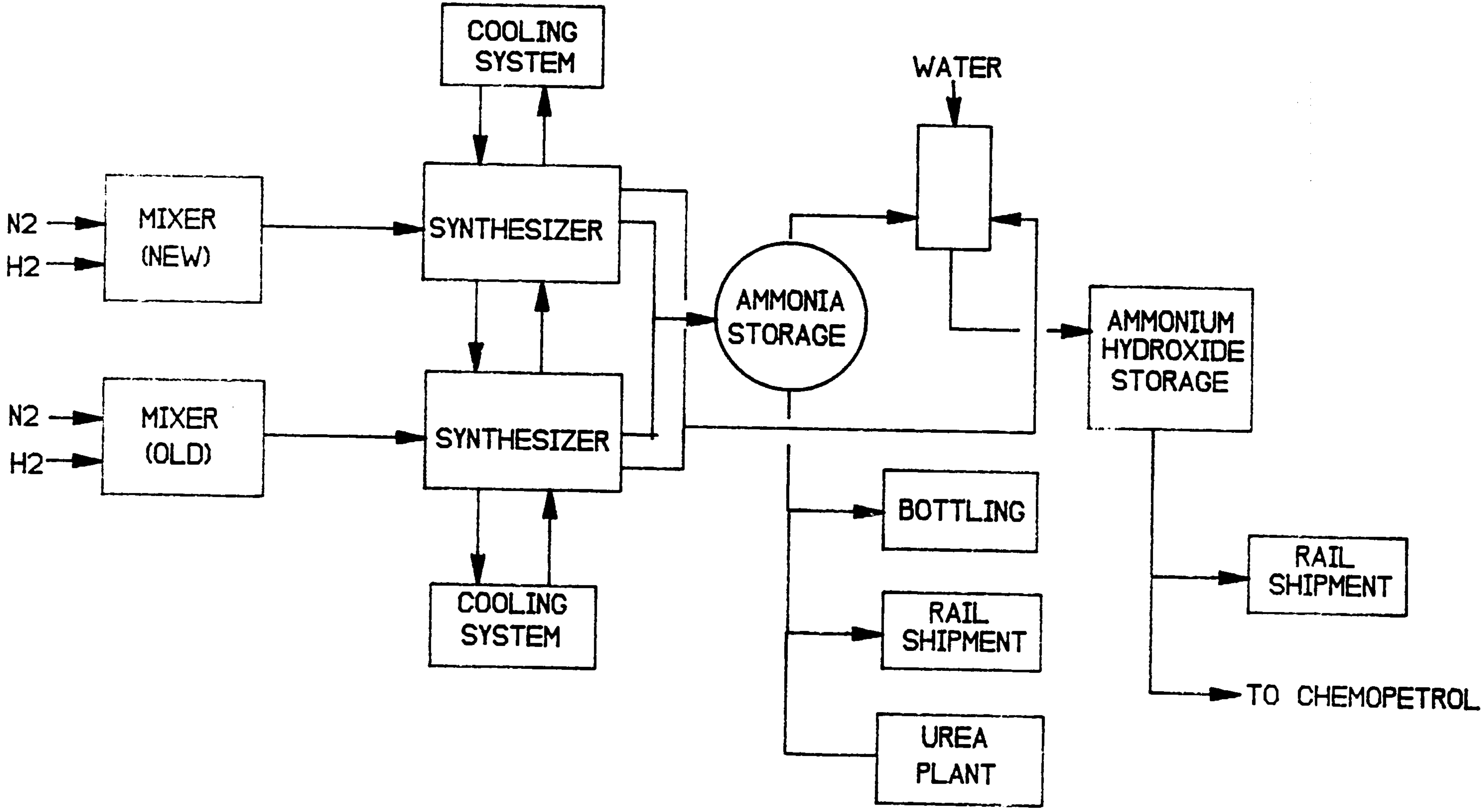
900
METHANISATION
DEOXIDATION ON
CATALYSTS

PSA
PARTITION OF GAS
ON MOLECULAR SIEVE

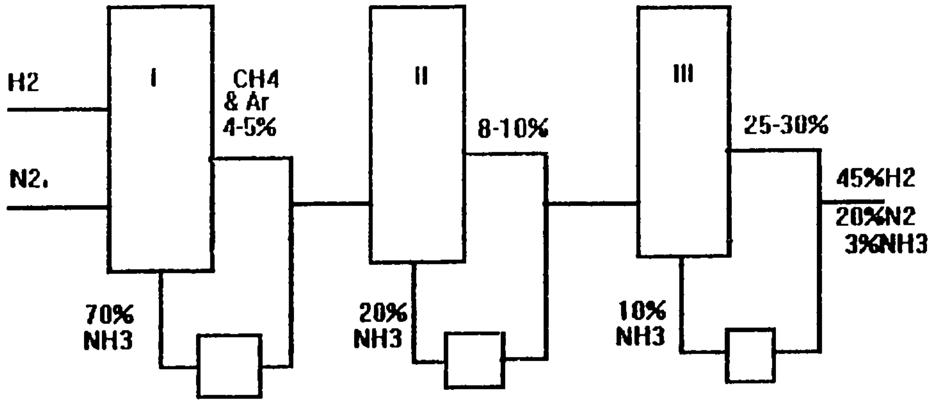
PRODUCTION OF CARBON BLACK



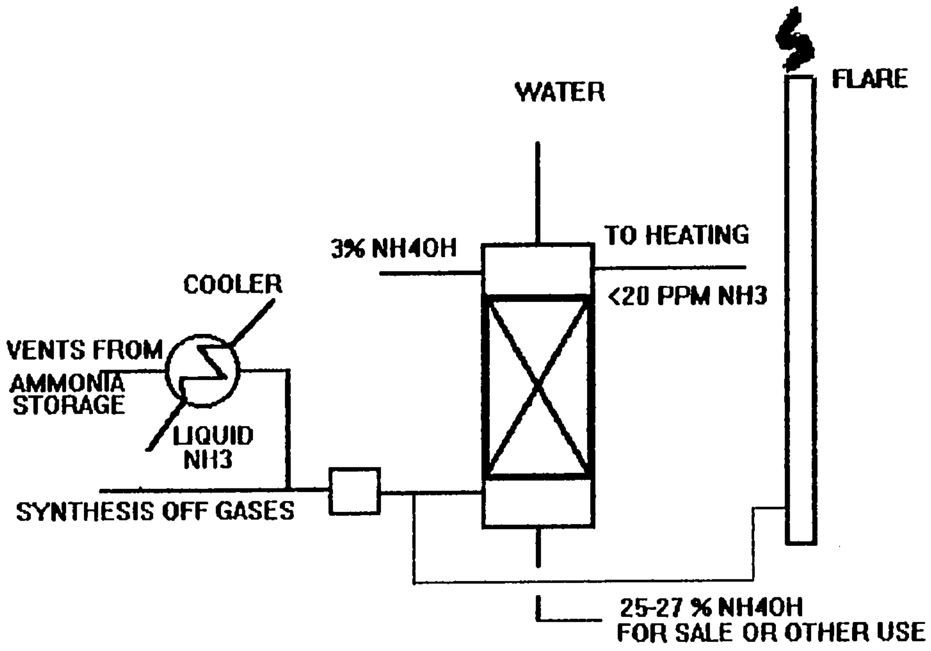
AMMONIA PRODUCTION PLANT



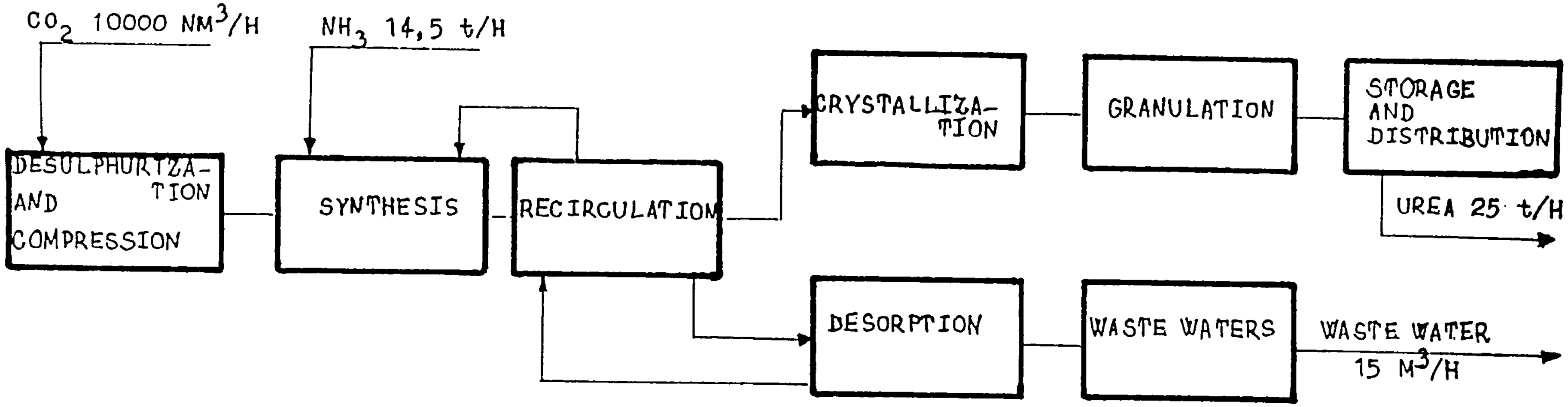
AMMONIA SYNTHESYS UNITS



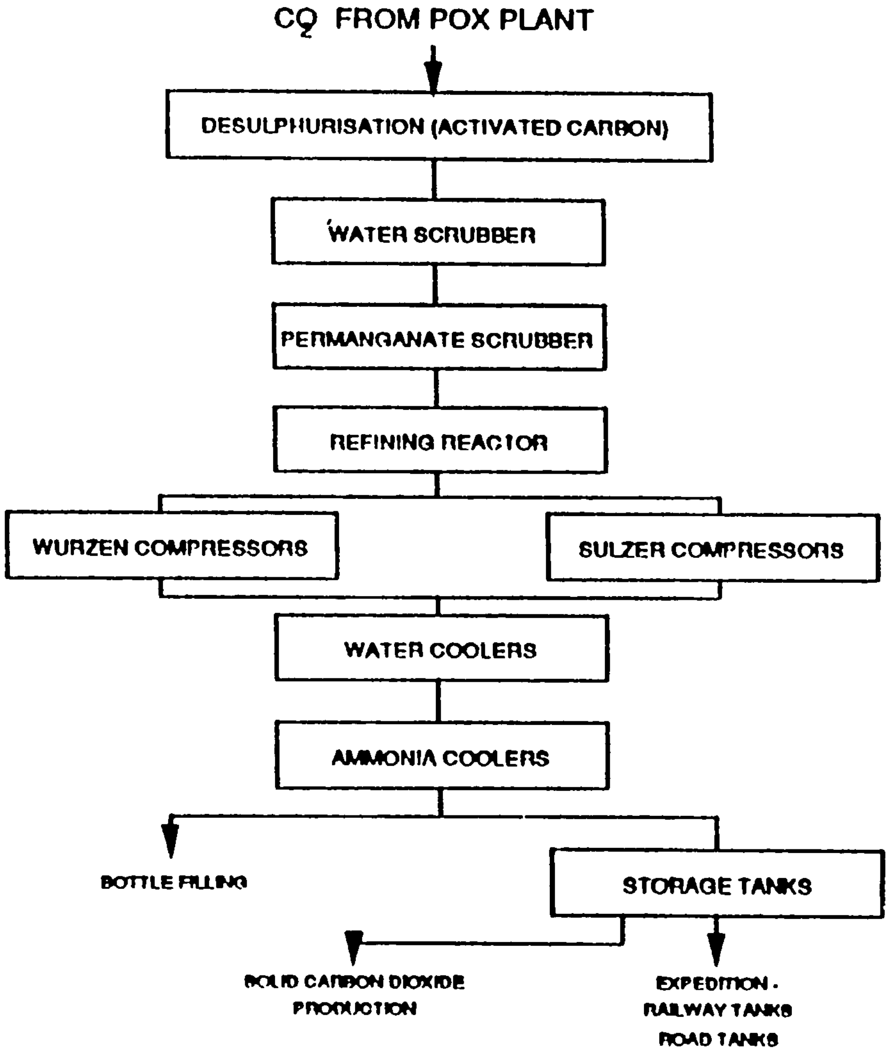
AMMONIA ABATEMENT



UREA PRODUCTION



Process Flows: Carbon Dioxide



CO_2 FROM POX PLANT

DESULPHURISATION (ACTIVATED CARBON)

WATER SCRUBBER

PERMANGANATE SCRUBBER

REFINING REACTOR

WURZEN COMPRESSORS

SULZER COMPRESSORS

WATER COOLERS

AMMONIA COOLERS

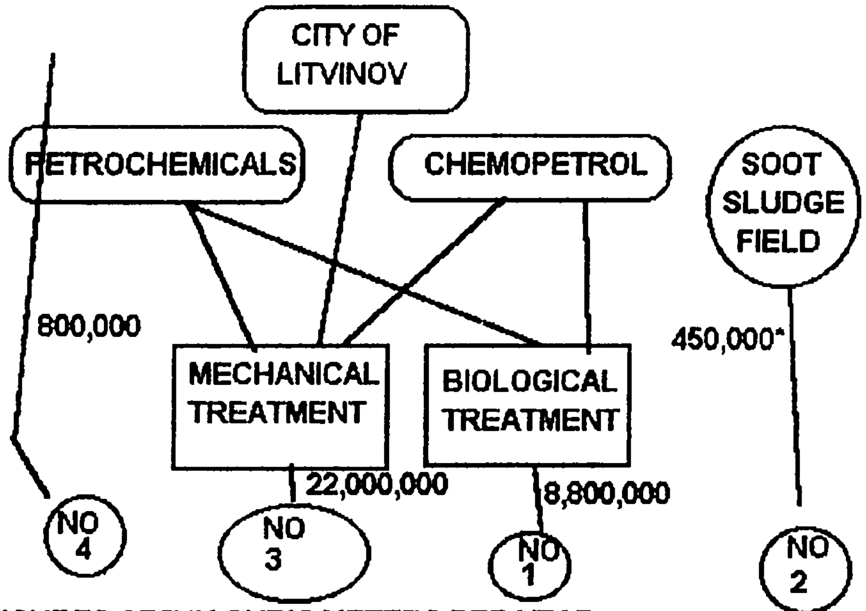
BOTTLE FILLING

STORAGE TANKS

SOLID CARBON DIOXIDE PRODUCTION

EXPEDITION -
RAILWAY TANKS
ROAD TANKS

WATER TREATMENT FACILITY AND WATER DISCHARGES TO RIVER BILINA



FIGURES ARE IN CUBIC METERS PER YEAR

APPENDIX C

TRAVEL ITINERARY

18 JUN 94	- SATURDAY			
AIR	DELTA AIR LINES INC.	FLT:1500	COACH	
	LV GAINESVILLE FL		230P	
	AR ATLANTA		335P	NON-STOP
AIR	DELTA AIR LINES INC.	FLT:20	BUSINESS	
	LV ATLANTA		530P	
19 JUN 94	- SUNDAY			
	AR FRANKFURT		825A	NON-STOP
AIR	DELTA AIR LINES INC.	FLT:58	BUSINESS	
	LV FRANKFURT		1210P	
	AR PRAGUE		130P	NON-STOP
02 JUL 94	- SATURDAY			
AIR	DELTA AIR LINES INC.	FLT:57	BUSINESS	
	LV PRAGUE		900A	
	AR FRANKFURT		1005A	NON-STOP
AIR	DELTA AIR LINES INC.	FLT:27	BUSINESS	
	LV FRANKFURT		205P	
	AR ATLANTA		535P	NON-STOP
AIR	DELTA AIR LINES INC.	FLT:1009	COACH	
	LV ATLANTA		710P	
	AR GAINESVILLE		815P	NON-STOP

APPENDIX D

Persons and Organization visited at Chemopetrol include the following individuals listed.

- **Chemopetrol Agro Division**

Ing. Petr Kubal	Division Head
Milan Ricanek, Ph. D.	Technical Director
Ing. Zdenek Hrzan	Chief of Technical Dept.
Mrs. Dana Ricankova	Department Chief - Quality Control
Mr. Miroslav Beranek	Technologist, Liquid CO_2 & Dry Ice Production
Mr. Radko Cihlar	Technologist of Urea Plant
Mr. Mikulas Huljak	Head, Carbon Black Production Unit
Mr. Milan Kane	Catalyst Plant Manager
Ing. Jan Konrad	Manager, Ammonia Synthesis
Mr. Jiri Loukota	Technologist of Partial Oxidation Plant
Mr. Jaromir Posival	Technologist of Partial Oxidation Plant
Mr. Otakar Soukup	Technologist of Oxygen Production Plant

- **Chemopetrol Environmental Protection Department**

Ing. Jaroslav Cir, CSc	Department Head
Ing. Danuse Brzobohata	Specialist

- **Chemopetrol Water and waste Division**

Ing. Jan Hurych	Technical Director
Mrs./Ing. Barbora Lancingerova	Water Treatment Plant Manager

- **Chemopetrol Research Institute**

Jaromir Lederer, Ph. D.	Director
Ing. Frantisek Necesany	Researcher
Petr Svoboda	Head of the Analytical Chemistry Department

APPENDIX E

(Copy of Business Cards of Persons Visited)

CHEMOPETROL

Ing. Petr Kubal
ředitel divize AGRO

CHEMOPETROL a. s.
436 70 Litvínov
Česká republika
☎ 035-33-4075, 2794
Fax: 035-33-4326

CHEMOPETROL
státní podnik LITVÍNOV

Ing. Jaroslav CÍR, CSc.
vedoucí odboru ochrany životního prostředí

CHEMOPETROL, s. p.
436 70 Litvínov
ČSFR
☎ 035-299-4515
Fax: 035-4734
Telex: 184278, 184333

CHEMOPETROL

Milan Říčánek PhD.
Technical Director of Division AGRO

CHEMOPETROL a. s.
436 70 Litvínov
CR
☎ 035-33 3496
Fax 035 33 4326

Privat
Alšova 984
436 01 Litvínov
☎ 035-533 79

CHEMOPETROL

Ing. Danuše Brzobohatá
specialista odboru ochrany životního prostředí - odpady

CHEMOPETROL a. s.
436 70 Litvínov, CR
☎ 035-33-4222
Fax: 035-282 24
Telex: 184278, 184333

CHEMOPETROL

Ing. Zdeněk HRZÁN
vedoucí technického oddělení divize AGRO

CHEMOPETROL, s. p.
436 70 Litvínov
Česká republika
☎ 035-33-3496
Fax 035-33-4326

CHEMOPETROL

Ing. Jan Hurych
Technical Director of Water & Wastes

CHEMOPETROL a. s.
436 70 Litvínov, CR
☎ 035 33-2685
Fax. 035-282 24, 333 905
Telex 184278, 184333

CHEMOPETROL

Ing. Jan KONRÁD
vedoucí výrobny syntéz NH_3 divize AGRO

CHEMOPETROL, s. p.
436 70 Litvínov
Česká republika
☎ 035-33-2469
Fax 035-33-4561

CHEMOPETROL

Milan Káně
Catalyst Plant Manager Division Agro

CHEMOPETROL a. s.
436 70 Litvínov
Czech Republic
☎ 0042-35-33-3344
Fax 0042-35-33-2677

APPENDIX E

(Copy of Business Cards of Persons Visited)

CHEMOPETROL

Research & Development Center

Jaromír LEDERER, Ph. D.
Director

CHEMOPETROL, s. p.
436 70 Litvínov
Czech Republic
☎ 42-35-33-3168
Fax: 42-35-33-4236
Telex: 184278, 184333

CHEMOPETROL
státní podnik LITVÍNOV

Dana ŘIČÁNKOVÁ
Department chief quality control

CHEMOPETROL, s. p.
436 70 Litvínov
ČSFR
☎ 42-035-299-3189
Fax: 42-035-4734
Telex: 184278, 184333

CHEMOPETROL

Výzkumné vývojové centrum

Ing. František NEČESANÝ
vedoucí odboru realizace výzkumu

CHEMOPETROL, s. p.
436 70 Litvínov
Česká republika
☎ 035-33-4320
Fax: 035-33-4236
Telex: 184278, 184333

CHEMOPETROL
státní podnik LITVÍNOV

Ladislav ŽENÍŠEK
odbor řízení jakosti

CHEMOPETROL, s. p.
436 70 Litvínov
33 ČSFR
☎ 035-[illegible]-3078
Fax: 035-4734
Telex: 184278, 184333

CHEMOPETROL
státní podnik LITVÍNOV

Petr SVOBODA, Ph.D.
Head of Analytical Chemistry Department

CHEMOPETROL, s. p.
Research & Development Center
436 70 Litvínov
Czech Republic
☎ 42-35-33-2709
Fax: 42-35-33-4236
Telex: 184278, 184333

APPENDIX F

List of document Received:

- Plant process flow sheets in Appendix A
- Chemopetrol Annual Report - 1993
- Chemopetrol Research Institute Brochure
- Chemopetrol Fold out Brochure
- Copies of Sections of Environmental Laws of the Czech Republic (examples attached including a table showing fees for disposal of wastes)
- Pilot plant test results of water purification using Chezacarb as an adsorber. (examples attached)

The Ministry of the Environment of the Czech Republic may, by Decree, define details on the classification of waste in the relevant groups of dumps given in the Appendix, which is an integral part of this Act.

§ 7

This Act comes into legal effect on April 1, 1992.

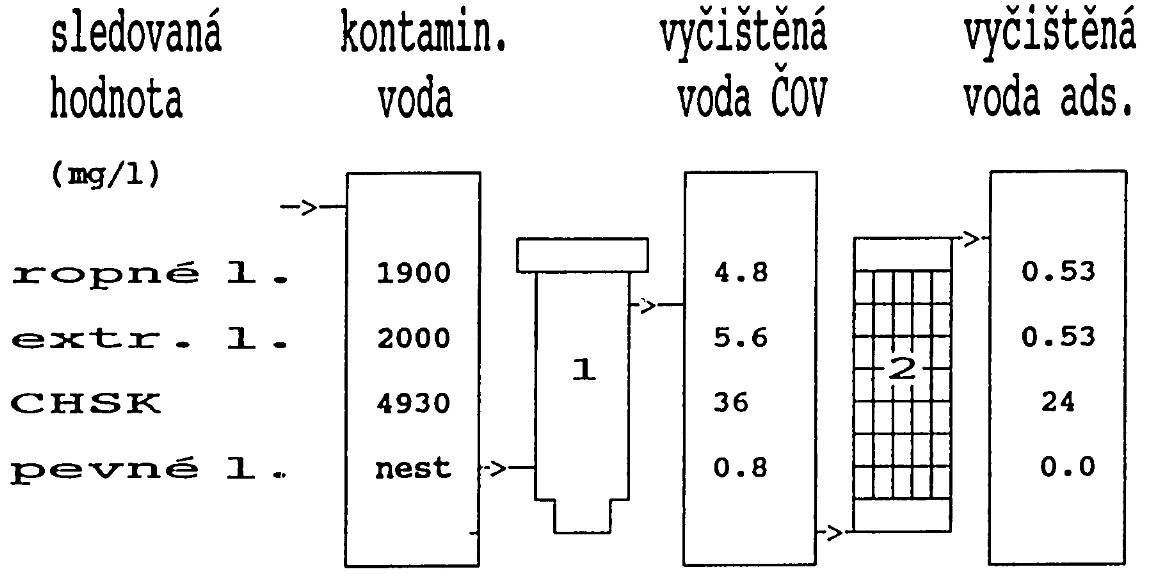
Signed: V.Burešová, P.Pithart

APPENDIX TO ACT No. 62/1992 S.B.

Rates of Charges for the Deposit of Waste on Waste Dumps

Groups of waste dumps	Rate I. (xt.$^{-1}$ Czech. Crowns)	Rate II. (xt.$^{-1}$ Czech. Crowns)		
		for 1992	1993	1994
1. Soil and gangue	0	1	3	6
2. Other (except soil and gangue)	10	25	70	140
3. Solid communal waste	20	20	70	210
4. Special waste (except hazardous and solid communal waste)	40	110	320	640
5. Hazardous waste	250	3 000	4 000	5 000

Čištění kontaminovaných vod směsi olejů a emulgátoru – stabilizované emulze s obsahem ropných látek do 2000 mg/l



sledovaná hodnota (mg/l)	kontamin. voda	vyčištěná voda ČOV	vyčištěná voda ads.
ropné l.	1900	4.8	0.53
extr. l.	2000	5.6	0.53
CHSK	4930	36	24
pevné l.	nest	0.8	0.0

Spotřeba Chezacarbu 880 g/m³

Legenda:

ap.č. 1 ČOV IRIS
ap.č. 2 adsorber s CHZC

APPENDIX G

BHASKAR BANDYOPADHYAY
8333 South West 4th. Place
Gainesville, Florida 32607
Home: (904) 332-3865 Work: (904) 397-8410

SUMMARY

A senior chemical engineering manager with a proven track record in the management of process and project engineering, production debottlenecking, R&D, pilot plant, energy and raw material conservation, quality assurance and Deming based Continuous Quality Improvement Process in industrial chemical environment. Production technology experience includes phosphate rock and limestone mining and processing, phosphoric acid and phosphatic fertilizer chemicals, chlorine/caustic, chloromethanes, chlorobenzene, EDC/VCM, synthetic soda ash and related, and furnace and foundry coke.

PROFESSIONAL EXPERIENCE

OCCIDENTAL CHEMICAL CORPORATION, Florida Operations, White Springs, Florida **1979-Present**

Technical Manager/Director

Directed the activities of Process Improvement, R&D/Technical Services, Project Engineering, Quality Assurance and Utilities Departments for cost and quality improvements at the phosphate fertilizer complexes.

- Collectively reduced production cost valued at over $40 million per year.
- Initiated and coordinated the implementation of Deming based Continuous Quality Improvement efforts throughout Florida Operations.
- Participated in the Corporate Water Issues Committee assisting with responsibly influencing the passage of the new Clean Water Act through the U.S. Senate.
- Initiated switching of electrical power contract at two chemical complexes from curtailable to interruptible rates reducing annual power cost by $1.5 million.
- Directed the development of an improved SPA product to increase domestic market share for this product.
- Managed the licensing of Oxy Hemihydrate™ Process.

ALLIED CHEMICAL CORPORATION **1968-1979**

Director, Research & Development, Semet-Solvay Division, Ironton, Ohio 1979

Directed divisional technical efforts to improve performance of Allied's Detroit and Ashland foundry and furnace coke plants.

- Initiated operational improvements at the two plants saving in excess of $2 million per year.

Technical Manager, Syracuse Works, Solvay, New York 1977-1979

Process Improvements Manager, Syracuse Works, Solvay, New York 1975-1977

Managed process improvement and development, quality control and energy resources departments at the facility which included mining and processing of limestone and production of synthetic soda ash and related products as well as electrolytic chlorine and caustic soda.

- Initiated numerous raw material and energy efficiency improvement projects achieving savings of $10 million per year.
- Eliminated fuel oil usage at the boilerhouse saving in excess of $1 million per year.

Senior Research Engineer, Syracuse Technical Center, Solvay, New York 1969-1975

Provided technical support to the chlorine/caustic plants at Solvay, N.Y. and Brunswick, GA and to the EDC/VCM plants at Baton Rouge, LA.

- Implemented closed loop computer control of the EDC cracking furnaces and the Oxyhydrochlorination reactor, increasing VCM production by 20%.
- Developed patented EDC cracking catalysts and patented low emission Oxyhydrochlorination process.
- Reduced, power usage in chlorine/caustic plants with DSA's.

Research Engineer, Research & Development, Morristown, N.J. 68-1969

Conducted bench scale exploratory studies on recovery of sulfur and metal values from pyrites using novel chelating techniques resulting in two U.S. patents.

EDUCATION

Doctor of Philosophy in Chemical Engineering 1969
Master of Science in Chemical Engineering 1967
Phil Lambda Upsilon & Sigma Xi Honor Societies
University of Pennsylvania, Philadelphia, PA.

Master of Technology in Food Technology (First Class Honors)	1964
Bachelor of Science in Chemical Engineering (First Class Honors)	1961

Jadavpur University, Calcutta, India

ASSOCIATIONS

Member, American Institute of Chemical Engineers
Past Chairman, Syracuse Section of AIChE
Member, President's Council, University of Florida
Past Member, Technical Advisory Committee, Florida Institute of Phosphate Research
Member, Board of Directors, Florida Institute of Phosphate Research (appointed by Governor Lawton Chiles)

ENVIRONMENTAL ADDENDUM
TO TRIP REPORT AUGUST 1994
BY B. BANDYOPADHYAY

concerning visit to:

Agro Division of Chemopetrol

Litvinov, Czech Republic June 20 - 30, 1994

prepared for

The World Environment Center

Wesley W. Atwood
Consulting Engineer
August 1994

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ATTACHMENTS

COMMENTS AND ENVIRONMENTAL DATA

concerning
visit to Agro Division
Chemopetrol, Litvinov, Czech Republic
June 20 - 30, 1994

I SUMMARY

The Chemopetrol facility at Litvinov, Czech Republic was visited during June 20 through 30, 1994 on a trip sponsored by the World Environment Center of New York. A high level of professionalism, environmental awareness and cooperation was found.

The purpose was to review and identify waste minimization opportunities in the AGRO Division. This addendum to the trip report August, 1994 by Dr. Bandyopadhyay covers:

- a review and comparison of water and air effluent limitations between the U. S. and Czech Republic
- comments on hazardous waste regulations and environmental aspects of urea and ammonia production
- recommendations
- copies of regulations, development documents, and pertinent technical papers relative to waste minimization.

The following environmental standards were compared:

1. Ambient air
2. Workplace
3. Air emissions
4. Liquid industrial effluents
5. Sanitary waste effluent
6. Surface water quality (receiving streams)

The Czech Republic environmental regulations, many adopted in the 1990's, appear more restrictive than those in the U. S. The effect of this on industry may or may not be mitigated by frequency of monitoring, analytical methods or enforcement posture. The overall impression, however, is that certain of the rules may be punitive.

Ambient air limits in particular are stringent with, for example, the 24 hour standard for sulfur dioxide set at only 40% of the U. S. In addition, workplace standards are also more stringent. On the other hand, water quality and effluent standards in general appear more lenient. There were many more standards than expected.

Hazardous waste "regulations" and compliance present the facility with complex, expensive issues which should justify assessment by an outside consulting firm.

For example, Vanadium was found present in a Czech water leach test on a Chemopetrol waste. It seemed to be a major determinant. Yet Vanadium is not even recognized as a hazardous waste contaminant that could be identified in the U. S. EPA leach test. The EPA "TCLP" Leach Test procedure is included for comparison.

In the discussion on specific environmental aspects, emissions are calculated based on the size of plants in the AGRO Division. These results are founded on extensive field test of plants in compliance by U. S. EPA, are reliable, and could be used as waste minimization goals.

At Chemopetrol common storm sewers efficiently collect all effluent. A recommendation is to consider segregation of contaminated water collection systems to allow treatment in smaller quantities for improved efficiency and reduced cost. Changes currently planned at the urea plant (restricted by capital) would be good starts.

Overall monitoring needs to be increased to "nail down" the source and fate of pollutants without which waste minimization can be impeded. A recommendation for ISCO automatic samplers has been included.

II AMBIENT AIR, WORKPLACE AND EFFLUENT LIMITATIONS

Ambient Air Quality Standards

During the visit, great interest was expressed in USA environmental limitations. While various Czech limitations were obtained, it has been difficult to make direct comparisons but they have been drawn where possible.

Table 1 draws this comparison for the six USA National Ambient Air Quality Standards. The Czech Republic lists a total of 30 standards, including many organics such as gasoline, xylene, ethylene.

Table 1 - Ambient Air Quality Standards For Criteria Air Pollutants(1)

	USA		Czech Republic	
Pollutant	Period	Limitation $\mu g/m^3$ (ppm)	Period	Limitation $\mu g/m^3$ (ppm)
Sulphur Dioxide	Annual Mean Max 24 Hr^2 Max 3 Hr avg.^{2}	80 (0.03) 365 (0.14) 1300 (0.50)	Annual Mean 24 Hr 30 Min	60 150 500
Particulates (PM-10)^3	Annual Mean Max 24 Hr^2	50 60	24 Hr 30 Min	150 500
Carbon Monoxide	Max 8 Hr^2 Max 1 Hr^2	10 (9) 40 (35)	24 Hr 30 Min	1000 6000
Photochemical Oxidants	Max 1 Hr^2	235 (0.12)	24Hr 30 Min	30 160
Nitrogen Dioxide	Annual Mean	100 (0.053)	24 Hr 30 Min	100 100
Lead	3 Mon. Mean	1.5		
Ammonia^4	<u>None Federal</u> A few states have regulations in the range of 1/4 to 2 1/2 ppm for 8 hours.		24 Hr 30 Min	200(0.3) 200

Status of Ammonia and Other Ambient USA Standards

Non-criteria pollutants as opposed to those in Table 1, have been the subject of much study. The information below on ammonia is an example of where non-criteria pollutant regulation stands.

Ammonia is considered toxic, but noncarcinogenic. It comes under Section 112 of the Clean Air Act. "Section 112 directs EPA to set uniform national emission limits with an ample margin of safety to protect human health against any non-criteria air pollutant which may result in increased mortality, serious irreversible or incapacitating reversible illness". EPA has not set a national standard for ammonia.

The Czech Republic ambient air standard for ammonia is 200 $\mu g/m^3$ for 30 minutes and 24 hours (0.3ppm) while the 8 hour workplace average is $20 mg/m^3$ (29 ppm).

Some states have been evaluating noncriteria air pollutants since 1979 (Texas has evaluated "probably 1000"). There has been limited Federal and state action (court tie-ups over safety factors on carcinogens) to produce enforceable ambient air limits. Emphasis is on carcinogens, and setting "guidelines" to assist permitting of new sources.

Footnotes for Table 1

(1) Definition: "A restriction established to limit the quantity or concentration of an air pollutant that may be allowed to exist in the ambient air for any specific period of time".

Comment: Above standards were established to protect public health. Some to also protect the public welfare, e.g. animal and plant life. All ambient standards are applicable at plant limits. Other states like Florida may have limits more stringent than Federal USA and then these are limiting for the plant. Some cities in USA also have more stringent standards than either state or Federal USA. e.g. California, nitrogen dioxide 0.25 ppm for one hour.

(2) Not to be exceeded more than once per year.

(3) PM-10 Definition: Particulates with aerodynamic diameter less than or equal to a nominal 10 micrometers.

(4) Czech Republic lists ambient air standards for 30 parameters - USA only six.

Only, seven states have ambient air ammonia regulations binding by law at plant limits. Ambient air concentrations range from 0.1 - 2.5 ppm for 8 hour average. Thirteen states have "guidelines" not binding by law at plant limits. Typical range of "guideline" values in the 13 states:

Average Time	PPM
Annual	0.06 - 2.5
24 hours	0.03 - 0.6
15 min.	4
30 min.	0.25
1 hour	0.6

There are no long-term low level epidemiological studies to support ambient air levels as low as above.

Work place standards for air contaminants

USA, under the Federal Occupational Safety and Health Administration (OSHA) lists federally enforceable limits on about 500 air contaminants. The Czech Republic lists 135.

Table 2 lists some comparisons. The Czech Republic is based on 8 hour averages; USA is based on a Time Weighted Average for an 8 hour work day, 5 days per week. On a random check of 12 substances, the permissable exposure limits in the Czech Republic are markedly lower than the U. S.(OSHA Reference Manual Volume 2, The Merritt Co., "OSHA Self Inspection Index)

Effluent Limitations

Air Emissions

Ammonia emissions from nitrogen fertilizer plants (urea, ammonia, etc.) are usually of minor importance under proper operating conditions. However, various states control particulate emissions. There are no Czech ammonia or particulate emission limitations for ammonia or urea plants.

Urea particulate emissions are limited in 16 U. S. states. Based on an average of these limits, the Chemopetrol urea plant at 200,000 TPY (330 days) would be allowed 0.55 Kg/Mg of product.

Attachment 1, (U. S. EPA 1992) Table 6.14-1 summarizes the controlled and uncontrolled emission factors by process for urea manufacture. It is based on a number of EPA sponsored tests at five plants in the U. S. but has not become an EPA regulation.

For fluidized bed prilled urea, it shows an uncontrolled particulate emission of 3.1 Kg/Mg and a controlled emission of 0.39 Kg/Mg. It also shows an uncontrolled ammonia emission of 1.46 Kg/Mg. Control was by wet scrubbers. No ammonia control was demonstrated by the wet scrubbers.

Table 2 - Workplace Standards (mg/m^3)

SUBSTANCE	USA	CZECH REPUBLIC
Ammonia NH_3	35	20
Hydrogen Fluoride HF	3.6	1
Formaldehyde HCHO	2.4	0.5
Ethyl Alcohol C_2H_5OH	1900	1000
Ethyl Benzene $C_6H_5C_2H_2$	435	200
Sulfur Dioxide SO_2	13	5
Carbon Monoxide CO	55	30
Carbon Dioxide CO_2	9000	9000
Ozone O_3	0.2	0.1
Sulfur Trioxide SO_2	1.0 (H_2SO_4)	1.0
Hydrogen Cyanide HCN	11	3.0
Carbon Black C	3.5	None (?)

Table 3 - Liquid Effluent Limitations for Nitrogen Fertilizer Plants

TYPE OF PLANT	PARAMETER	LIMITATION Kg/Mg of Product	
		Daily Max	Average of 30 Consecutive days
Ammonia	Ammonia as N	0.11	0.055
Urea			
Non-prilled	Ammonia as N	0.53	0.27
Prilled	Ammonia as N	0.53	0.27
Non-prilled	Organic N as N	0.45	0.24
Prilled	Organic N as N	0.86	0.46

Currently in the regulatory process under the U.S. Clean Air Act, Section 112r, (amended in 1990) is an Accidental Release Prevention requirement. Initially it covers 100 chemicals including ammonia and aqueous ammonia. It requires the manufacturer to do a hazard assessment followed by a risk management plan. A "worst case" is being defined for the hazard assessment as part of this regulatory process. This may take several years.

Liquid Effluents

Table 3 lists U. S. EPA regulations for liquid effluents from ammonia and urea plants. They include rainfall run-off from the immediate vicinity ("battery limits") of the urea or ammonia plant. There are no Czech limitations for ammonia or urea plants. To my knowledge, at no time during the visit to Chemopetrol did we discuss organic nitrogen as part of the overall nitrogen picture.

Secondary Sanitary Waste Treatment Regulations

All sewage treatment plants in the U. S. must meet the following "minimum level of effluent quality attainable by secondary treatment in terms of the parameters BOD_5, SS and pH".

Table 4 - Federal Sanitary Waste Effluent Regulations

	Average	Maximum	Minimum Average Percent Removal
BOD_5	30 day 7 day	30 mg/l 45 mg/l	85
Suspended Solids	30 day 7 day	30 mg/l 45 mg/l	85
pH	6 - 9 units		

It is noted that where sanitary sewage treatment works receive flows from storm water and/or industrial wastes, requirements are set on a case-by-case basis. Also, additional, more stringent regulations are often imposed by state and local governments.

For example, secondary treatment of sanitary waste in Florida requires a BOD_5 of 20 mg/l and suspended solids of 20 mg/l with fecal coliform, after disinfection, not to exceed 200 per 100 ml of water on a monthly average.

Advanced Water Treatment (AWT) that may use land spreading or spraying to remove nutrients (N and P) is increasingly employed. Florida requires the following parameters to be met for AWT which is required on a case-by-case basis.

BOD5	5 mg/l
Suspended Solids	5 mg/l
Total Nitrogen (N)	3 mg/l
Total Phosphorous	1 mg/l
High level disinfection	fecal coliform not detectible

Chemopetrol meets the following limits with a combined sanitary waste, storm water and industrial waste effluent.

$N(NH_4)$	5 - 10 mg/l
BOD_5	8 - 10 mg/l

Chemopetrol also monitors and reports on suspended solids, chemical oxygen demand, total dissolved solids and phosphates (as P). Czech Republic waste requirements are:

BOD	45 mg/l
COD	150 mg/l
Suspended Solids	35 mg/l
Ammonia N	25 mg/l

This is similar to secondary treatment in the U. S. although the ammonia N would be considered high.

Surface water quality regulations

Attachment 2 covers the quality required in receiving streams in Florida and includes a similar list for the Czech Republic. Most streams in Florida are Class III waters suitable for recreation, propagation and maintenance of a healthy, well balanced population of fish and wildlife. Florida is among those states with the most stringent regulations. Note that heavy metals, herbicides, pesticides, and many organics are included.

Particular attention is paid to unionized ammonia restricted to 0.02 mg/l. This value is a function of ammonia N (expressed as NH_3) pH, and temperature.

For example, at a pH of 7, temperature of 10°C, and a total ammonia of 11 mg/l (9 mg/l of N) the unionized ammonia will reach 0.02 mg/l. U. S. EPA (1976) Attachment 3, explains the importance of unionized ammonia in receiving waters.

Table 5 compares some of the Czech Republic water quality regulations with those of Florida. It is not known if Chemopetrol discharges into "water-works" or "other surface waters" which are obviously less restrictive.

Table 5 - Surface Water Quality Regulations (Partial List)

Parameter	Units	Florida Class III Waters (Attachment 5)	Czech Republic (Attachment 6)	
			Value Water Works	Value Other Surface Waters
Dissolved Oxygen	mg/l	5 Min	6 Min	4 Min
Arsenic - A s	µg/l	50	50	100
Benzene - BZ	µg/l	71 Annual Avg.	10	50
Cyanide - CN	µg/l	5	Not Detectable (ND)	200
Cadmium - Cd	µg/l	~10	5	15
Chromium VI - Ct^{6}	µg/l	11	20	50
Mercury - Hg	µg/l	0.012	0.5	1.0
Silver - Ag	µg/l	0.07	10	50
Selenium - SE	µg/l	5	10	50
Fluorides - F	mg/l	10	1.0	1.5
Nutrients	mg/l	No Values "Case-by Case"		
Organic N	mg/l	"	1.5	3.0
N - NH_4^+	mg/l	"	0.5	2.5
N - NO_2	mg/l	"	0.02	0.05
N- NO_3	mg/l	"	3.4	11.0
Total P	mg/l	"	0.15	0.4
Pesticides and Herbicides	µg/l	Many Listed	None Listed	

III HAZARDOUS WASTE REGULATIONS

U. S. regulations cover listed hazardous wastes which include both compounds and mixtures, and characteristic hazardous wastes.

Hazardous wastes are categorized as follows:

Ignitable Waste
Corrosive Waste
Reactive Waste
Toxicity Characteristic Waste
Acute Hazardous Waste
Toxic Waste

A solid waste exhibits the characteristic of toxicity if using specified leach test methods the extract from a representative sample of the waste contains any of the contaminants listed in Table 6. Attachment 4 describes the Toxicity Characteristic Leaching Procedure (TCLP).

At Chemopetrol, discussion included sludge field waste: a mixture of sanitary sludge, fly ash, soot water, and POX discharge containing ammonia. By a water leach test under the Czech Inspector for Environmental Protection (CIEP), this mixture was said to be toxic because of the presence of Vanadium and Arsenic in a leach test of the input streams.

Observations:

(1) U. S. regulations do not include the element Vanadium as a hazardous waste contaminant (Table 6). The closest is the "listed" relatively pure form of Vanadium Pentoxide (V_2O_5).

(2) Arsenic is included as a contaminant but based on the Tabulka from Chemopetrol it measured far below the regulatory level of 5 mg/l in the CIEP leach test at 0.072 mg/l.

(3) Flyash from coal burning is not normally a hazardous waste in the U. S.

(4) In the U. S. on a similar situation a company would hire an EPA approved expert consulting firm to sample the mixed waste in an EPA approved manner and to run the EPA approved TCLP leach test. If a contaminant was found, its source would be identified and hopefully isolated and treated and disposed before it could contaminate the larger waste stream.

Table 6 - Maximum Concentration of Contaminants for the Toxicity Characteristic (TCLP Leach Test)

EPA HW No.[1]	Contaminant	CAS No.[2]	Regulatory Level (mg/L)
D004	Arsenic	7440-38-2	5.0
D005	Barium	7440-39-3	100.0
D018	Benzene	71-43-2	0.5
D006	Cadmium	7440-43-9	1.0
D019	Carbon tetrachloride	56-23-5	0.5
D020	Chlordane	57-74-9	0.03
D021	Chlorobenzene	108-90-7	100.0
D022	Chloroform	67-66-3	6.0
D007	Chromium	7440-47-3	5.0.
D023	o-Cresol	95-48-7	[4]200.0
D024	m-Cresol	108-39-4	[4]200.0
D025	p-Cresol	106-44-5	[4]200.0
D026	Cresol		[4]200.0
D016	2,4-D	94-75-7	10.0
D027	1,4-Dichlorobenzene	106-46-7	7.5
D028	1,2-Dichloroethane	107-06-2	0.5
D029	1,1-Dichloroethylene	75-35-4	0.7
D030	2,4-Dinitrotoluene	121-14-2	[3]0.13
D012	Endrin	72-20-8	0.02
D031	Heptachlor (and its epoxide)	76-44-8	0.008
D032	Hexachlorobenzene	118-74-1	[3]0.13
D033	Hexachlorobutadiene	87-68-3	0.5
D034	Hexachloroethane	67-72-1	3.0
D008	Lead	7439-92-1	5.0
D013	Lindane	58-89-9	0.4
D009	Mercury	7439-97-6	0.2
D014	Methoxychlor	72-43-5	10.0
D035	Methyl ethyl ketone	78-93-3	200.0
D036	Nitrobenzene	98-95-3	2.0
D037	Pentrachlorophenol	87-86-5	100.0
D038	Pyridine	110-86-1	[3]5.0
D010	Selenium	7782-49-2	1.0
D011	Silver	7440-22-4	5.0
D039	Tetrachloroethylene	127-18-4	0.7
D015	Toxaphene	8001-35-2	0.5
D040	Trichloroethylene	79-01-6	0.5
D041	2,4,5-Trichlorophenol	95-95-4	400.0
D042	2,4,6-Trichlorophenol	88-06-2	2.0
D017	2,4,5-TP (Silvex)	93-72-1	1.0
D043	Vinyl chloride	75-01-4	0.2

[1] Hazardous waste number.

[2] Chemical abstracts service number.

[3] Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.

[4] If o-, m-, and p-Cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level of total cresol is 200 mg/l.

IV COMMENTS ON SPECIFIC ENVIRONMENTAL ASPECTS

Urea Production - Air Emission

The plant reports a loss to the air of between 180 and 314 TPY of urea dust.

Based on best data found by U. S. EPA (1992) in Section I, Air Emissions, a controlled emission factor of 0.39 Kg/Mg of product urea can be expected using wet scrubbers. On this basis, emission could be reduced to 78 TPY (200,000 TPY x 0.39 Kg/Mg ÷ 1000). This could be set as a potential goal.

The emission factor on NH_3 loss was found to be 1.46 Kg/Mg or 292 TPY. This would represent a very small part of the ammonia usage of 595 Kg/Mg (1/4%). Thus, with or without a wet prill tower scrubber, the ammonia loss appears almost entirely water related.

Urea Production - Liquid Effluent

The plant reports a loss to water from the Urea plant of 550 TPY of N (670 TPY NH_3) which reports to Biological Treatment #3. Based on raw material usage numbers the loss could be far higher when comparing a typical usage of 580 Kg/Mg to the reported 595 Kg/Mg of product.

Based on U. S. effluent regulations (Table 3), a prilled urea plant is limited to ammonia as N of 0.27 Kg/Mg of product; and organic N of 0.46 Kg/Mg of product or a total N of 0.73 Kg/Mg on a 30 day average.

Thus, it would seem possible, certainly as a goal, to reduce ammonia N to 54 TPY and total N (from both urea and ammonia) to 146 TPY based on an operating rate of 200,000 TPY.

To my knowledge, organic N content of urea plant effluent was not discussed. In U. S., the determination would be made by running Total Kheldahl Nitrogen and subtracting ammonia N to get organic N, an estimate of urea content as opposed to just ammonia.

Ammonia Production - Liquid Effluent

Based on U. S. effluent regulations (Table 3) an ammonia plant is limited to an effluent containing no more than 0.055 Kg/Mg. At 330,000 TPY of NH_3, this would be 18 TPY of ammonia N. This could be considered a goal in sampling the ammonia plant effluent.

Urea Production - Environmental Projects

U. S. plants control emissions of prill towers, have retention tanks or ponds, and urea hydrolyzers or equivalent. Otherwise, U. S. effluent limitations could not be met.

Hydrolyzers to recover urea and reduce contamination are planned at the Chemopetrol plant. This should proceed in order to reduce ammonia and organic N. The use of hydrolyzers were anticipated by U. S. EPA and considered state-of-the-art in 1974 which helped set effluent limits in 1977 (Table 3). Also, demonstrated at that time were steam and air stripping and biological treatment for nitrogen removal. Chemopetrol, of course, employs biological treatment. (Basic Fertilizer Chemicals, March 1974, EPA-440/1-74-011-a).

Attachment 5 is a technical paper by Killen of Vistron dated 1976, which discusses urea plant pollution control in general and difficulties with a C and I Girdler designed hydrolyzer. Wash down, and reclaiming systems for urea were highlighted.

V RECOMMENDATIONS

1. Consider recommendations proposed by Dr. Bandyopadhyay in Section I and V of his report.

2. Consider design of contaminated water collection systems so that common contaminant streams can be segregated and treated in smaller quantities for improved efficiencies and reduced treatment cost. This is especially applicable to the Urea plant - a major source of ammonia and organic N.

3. See Attachment 5 outlining some measures necessary and now used to meet effluent standards from urea plant battery limits. (As Dr. Bandyopadhy proposes, a consultant, or Chemopetrol team should perform a complete material and energy balance around the Urea plant).

4. Throughout, Chemopetrol needs to increase effluent monitoring - more and better sampling and flow metering. Better material and waste balances and more uniform and agreed upon reporting among divisions is needed. This will help "nail down" the source and fate of pollutants without which waste minimization can be impeded.

5. Automatic samplers can help. Occidental uses the ISCO Model 2910 sampler for both official discharge samples and for process troubleshooting or in-plant monitoring. These will take one sample per hour, for 24 hours, up to 100 ml each and can be iced or heated; even a flow proportioned sampler is available. (ISCO, Inc. 531 Westgate Blvd., Lincoln, Nebraska, USA, 68528; Phone: 800-228-4373; FAX: 402-474-6685)

6. On ammonia N samples, check on use of preservative (H_2SO_4) and refrigeration on any samples held for analysis. This may be a reason for <u>low</u> ammonia N values. Also analyze for Organic N.

7. Consider a consulting firm to examine the waste situation in the "sludge field". This seems very complex. In the U. S. "flyash" or sanitary sludge is seldom a hazardous waste; "Vanadium" is not a listed contaminant in the U. S. Toxicity Characteristic Leaching Procedure but seems to be a prime indicator of hazardous waste by CIEP at Chemopetrol.

   Considering the fees, new capital requirements, operating costs, and possible retrofit costs a thorough expert look should be justified. A U. S. facility would certainly employ an expert outside firm to make an assessment on this kind of situation and to interface with U. S. EPA if necessary.

8. Establish some unofficial goals for reduction of emissions. For example, note measured emissions from U. S. urea plants in Section II of this addendum. These values could help to provide goals and also to lend perspective for management.

ATTACHMENT 1

BACKGROUND REPORT

AP-42 SECTION 6.14

UREA

Prepared for

U.S. Environmental Protection Agency
OAQPS/TSD/EIB
Research Triangle Park, NC 27711

December 1, 1992
1-96

Pacific Environmental Services, Inc.
PO Box 12077
Research Triangle Park, NC 27709
919/941-0333

TABLE 6.14-1 (METRIC UNITS)
EMISSION FACTORS FOR UREA PRODUCTION

All Emission Factors are in kg/Mg of Product (x 2 = #/ton)
Ratings (A-E) Follow Each Factor

Type of Operation	Particulate[a]				Ammonia			
	Uncontrolled		Controlled		Uncontrolled		Controlled[g]	
Solution formation and concentration[b]	0.0105[c]	A			9.23[d]	A		
Nonfluidized bed prilling								
Agricultural grade[e]	1.9	A	0.032[f]	A	0.43	A		
Feed grade[h]	1.8	A						
Fluidized bed prilling								
Agricultural grade[h]	3.1	A	0.39	A	1.46	A		
Feed grade[h]	1.8	A	0.24	A	2.07	A	1.04	A
Drum granulation[i]	120	A	0.115	A	1.07[j]	A		
Rotary drum cooler	3.89[k]	A	0.10[l]	E	0.0256[k]	A		
Bagging	0.095[l]	E						

[a] Particulate test data were collected using a modification of EPA Reference Method 3. Reference 1, Appendix B explains these modifications.

[b] References 9 and 11. Emissions from the synthesis process are generally combined with emissions from the solution concentration process and vented through a common stack. In the synthesis process, some emission control is inherent in the recycle process where carbamate gases and/or liquids are recovered and recycled.

[c] EPA test data indicated a range of 0.005 to 0.016 kg/Mg (0.010 to 0.032 lb/ton).

[d] EPA test data indicated a range of 4.01 to 14.45 kg/Mg (8.02 to 28.90 lb/ton).

[e] Reference 12. These factors were determined at an ambient temperature of 14 to 21°C (57° to 69°F). The controlled emission factors are based on ducting exhaust through a downcomer and then a wetted fiber filter scrubber achieving a 98.3 percent efficiency. This represents a higher degree of control than is typical in this industry.

[f] Only runs two and three were used (test Series A).

[g] No ammonia control demonstrated by scrubbers installed for particulate control. Some increase in ammonia emissions exiting the control device was noted.

[h] Reference 11. Feed grade factors were determined at an ambient temperature of 29°C (85°F) and agricultural grade factors at an ambient temperature of 27°C (80°F). For fluidized bed prilling, controlled emission factors are based on use of an entrainment scrubber.

[i] References 8 and 9. Controlled emission factors are based on use of a wet entrainment scrubber. Wet scrubbers are standard process equipment on drum granulators. Uncontrolled emissions were measured at the scrubber inlet.

[j] EPA test data indicated a range of 0.955 to 1.20 kg/Mg (1.90 to 2.45 lb/ton).

[k] Reference 10.

[l] Reference 1. Data were provided by industry.

CZECH R[illegible]
"INDICATE 3" 1992

17-302.530, Criteria for Surface Water Quality Classifications (FLORIDA, USA)

(CURRENT AUGUST 1994)

	Parameter	Units	Class I: Potable Water Supply	Class II: Shellfish Propagation or Harvesting	Class III: Recreation, Propagation and Maintenance of a Healthy, Well-Balanced Population of Fish and Wildlife		Class IV: Agricultural Water Supplies	Class V: Navigation, Utility, and Industrial Use
					Predominantly Fresh Waters	Predominantly Marine Waters		
—	(1) Alkalinity	Milligrams/L as $CaCO_3$	Shall not be depressed below 20		Shall not be depressed below 20		≤ 600	
—	(2) Aluminum	Milligrams/L		≤ 1.5		≤ 1.5		
Not Det.	(3) Ammonia (un-ionized)	Milligrams/L as NH_3	≤ 0.02		≤ 0.02			
	(4) Antimony	Micrograms/L	≤ 14.0	≤ 4,300	≤ 4,300	≤ 4,300		
50-100	(5) (a) Arsenic (total)	Micrograms/L	≤ 50	≤ 50	≤ 50	≤ 50	≤ 50	≤ 50
—	(5) (b) Arsenic (trivalent)	Micrograms/L		≤ 36		≤ 36		

"Value for other surface waters"

"Value for waterworks water courses"

WB 8/12/94

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "ln H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

ATTACHMENT 2

	Parameter	Units	Class I	Class II	Class III: Fresh	Class III: Marine	Class IV	Class V
0.2-1.0	(10) Beryllium	Micrograms/L	≤ 0.0077 annual avg.	≤ 0.13 annual avg.	≤ 0.13 annual avg.	≤ 0.13 annual avg.	≤ 100 in waters with a hardness in mg/L of $CaCO_3$ of less than 250 and shall not exceed 500 in harder waters	
—	(11) Biological Integrity	Per cent reduction of Shannon-Weaver Diversity Index	The Index for benthic macroinvertebrates shall not be reduced to less than 75% of background levels as measured using organisms retained by a U. S. Standard No. 30 sieve and collected and composited from a minimum of three Hester-Dendy type artificial substrate samplers of 0.10 to 0.15 m^2 area each, incubated for a period of four weeks.	The Index for benthic macroinvertebrates shall not be reduced to less than 75% of established background levels as measured using organisms retained by a U. S. Standard No. 30 sieve and collected and composited from a minimum of three natural substrate samples, taken with Ponar type samplers with minimum sampling area of 225 cm^2.	The Index for benthic macroinvertebrates shall not be reduced to less than 75% of established background levels as measured using organisms retained by a U. S. Standard No. 30 sieve and collected and composited from a minimum of three Hester-Dendy type artificial substrate samplers of 0.10 to 0.15 m^2 area each, incubated for a period of four weeks.	The Index for benthic macroinvertebrates shall not be reduced to less than 75% of established background levels as measured using organisms retained by a U. S. Standard No. 30 sieve and collected and composited from a minimum of three natural substrate samples, taken with Ponar type samplers with minimum sampling area of 225 cm^2.	≤ 4.42 annual avg.	
1-3	(12) BOD (Biochemical Oxygen Demand)		Shall not be increased to exceed values which would cause dissolved oxygen to be depressed below the limit established for each class and, in no case, shall it be great enough to produce nuisance conditions.					
0.3-0.5	(13) Boron	Milligrams/L					≤ 0.75	
—	(14) Bromates	Milligrams/L		≤ 100		≤ 100		
—	(15) Bromine (free molecular)	Milligrams/L		≤ 0.1		≤ 0.1		

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "ln H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

	Parameter	Units	Class I	Class II	Class III: Fresh	Class III: Marine	Class IV	Class V
✓?	(6) Bacteriological Quality (Fecal Coliform Bacteria)	Number per 100 ml (Most Probable Number (MPN) or Membrane Filter (MF))	MPN or MF counts shall not exceed a monthly average of 200, nor exceed 400 in 10% of the samples. Monthly averages shall be expressed as geometric means based on a minimum of 5 samples taken over a 30 day period.	MPN shall not exceed a median value of 14 with not more than 10% of the samples exceeding 43	MPN or MF counts shall not exceed a monthly average of 200, nor exceed 400 in 10% of the samples, nor exceed 800 on any one day. Monthly averages shall be expressed as geometric means based on a minimum of 10 samples taken over a 30 day period.	MPN or MF counts shall not exceed a monthly average of 200, nor exceed 400 in 10% of the samples, nor exceed 800 on any one day. Monthly averages shall be expressed as geometric means based on a minimum of 10 samples taken over a 30 day period.		
✓?	(7) Bacteriological Quality (Total Coliform Bacteria)	Number per 100 ml (Most Probable Number (MPN) or Membrane Filter (MF))	≤ 1,000 as a monthly avg., nor exceed 1,000 in more than 20% of samples examined during any month, nor exceed 2,400 at any time, using either MPN or MF counts.	Median MPN shall not exceed 70, and not more than 10% of the samples shall exceed an MPN of 230.	≤ 1,000 as a monthly average; nor exceed 1,000 in more than 20% of the samples examined during any month; ≤ 2,400 at any time. Monthly averages shall be expressed as geometric means based on a minimum of 10 samples taken over a 30 day period, using either the MPN or MF counts.	≤ 1,000 as a monthly average; nor exceed 1,000 in more than 20% of the samples examined during any month; ≤ 2,400 at any time. Monthly averages shall be expressed as geometric means based on a minimum of 10 samples taken over a 30 day period, using either the MPN or MF counts.		
—	(8) Barium	Milligrams/L	≤ 1					
10-50	(9) Benzene	Micrograms/L	≤ 1.18	≤ 71.28 annual avg.	≤ 71.28 annual avg.	≤ 71.28 annual avg.		

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "ln H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

Parameter	Units	Class I	Class II	Class III: Fresh	Class III: Marine	Class IV	Class V
(21) Chronic Toxicity (see definition in Section 17-302.200(3), F.A.C. and also see below, "Substances in concentrations which...")							
(22) Color, etc. (see also Minimum Criteria, Odor, Phenols, etc.)	Color, odor, and taste producing substances and other deleterious substances, including other chemical compounds attributable to domestic wastes, industrial wastes, and other wastes					Only such amounts as will not render the waters unsuitable for agricultural irrigation, livestock watering, industrial cooling, industrial process water supply purposes, or fish survival.	
(23) Conductance, Specific	Micromhos/cm	Shall not be increased more than 50% above background or to 1275, whichever is greater		Shall not be increased more than 50% above background or to 1275, whichever is greater		Shall not be increased more than 50% above background or to 1275, whichever is greater	Shall not exceed 4,000
(24) Copper	Micrograms/L	$Cu \leq e^{(0.8545[\ln H]-1.465)}$	≤ 2.9	$Cu \leq e^{(0.8545[\ln H]-1.465)}$	≤ 2.9	≤ 500	≤ 500
(25) Cyanide	Micrograms/L	≤ 5.2	≤ 1.0	≤ 5.2	≤ 1.0	≤ 5.0	≤ 5.0
(26) Definitions (see Section 17-302.200, F.A.C.)							
(27) Detergents	Milligrams/L	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "ln H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

	Parameter	Units	Class I	Class II	Class III: Fresh	Class III: Marine	Class IV	Class V
5-15	(16) Cadmium	Micrograms/L	Cd $\le e^{(0.7852[\ln H]-3.49)}$; 10 max	≤ 9.3	Cd $\le e^{(0.7852[\ln H]-3.49)}$	≤ 9.3		
—	(17) Carbon tetrachloride	Micrograms/L	≤ 0.25 annual avg.; 3.0 max	≤ 4.42 annual avg.	≤ 4.42 annual avg.	≤ 4.42 annual avg.		
150-350	(18) Chlorides	Milligrams/L	≤ 250	Not increased more than 10% above normal background. Normal daily and seasonal fluctuations shall be maintained.		Not increased more than 10% above normal background. Normal daily and seasonal fluctuations shall be maintained.		In predominantly marine waters, not increased more than 10% above normal background. Normal daily and seasonal fluctuations shall be maintained.
ND-.05	(19) Chlorine (total residual)	Milligrams/L	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01		
	(20) (a) Chromium (trivalent)	Micrograms/L	Cr (III) $\le e^{(0.819[\ln H]+1.561)}$	$\le 673{,}000$	Cr (III) $\le e^{(0.819[\ln H]+1.561)}$	$\le 673{,}000$	Cr (III) $\le e^{(0.819[\ln H]+1.561)}$	In predominantly fresh waters, $\le e^{(0.819[\ln H]+1.561)}$. In predominantly marine waters, $\le 673{,}000$
20-50	(20) (b) Chromium (hexavalent)	Micrograms/L	≤ 11	≤ 50	≤ 11	≤ 50	≤ 11	In predominantly fresh waters, ≤ 11. In predominantly marine waters, ≤ 50

100-200 Total Cr

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "ln H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

Parameter	Units	Class I	Class II	Class III: Fresh	Class III: Marine	Class IV	Class V
(36) (a) Halomethanes (Total trihalomethanes) (total of bromoform, chlorodibromomethane, dichlorobromomethane, and chloroform). Individual halomethanes shall not exceed (b)1. to (b)5. below.	Micrograms/L	≤100					
(36) (b) 1. Halomethanes (individual): Bromoform	Micrograms/L	≤4.3 annual avg.	≤360 annual avg.	≤360 annual avg.	≤360 annual avg.		
(36) (b) 2. Halomethanes (individual): Chlorodibromomethane	Micrograms/L	≤0.41 annual avg.	≤34 annual avg.	≤34 annual avg.	≤34 annual avg.		
(36) (b) 3. Halomethanes (individual): Chloroform	Micrograms/L	≤5.67 annual avg.	≤470.8 annual avg.	≤470.8 annual avg.	≤470.8 annual avg.		
(36) (b) 4. Halomethanes (individual): Chloromethane (methyl chloride)	Micrograms/L	≤5.67 annual avg.	≤470.8 annual avg.	≤470.8 annual avg.	≤470.8 annual avg.		

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "ln H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

	Parameter	Units	Class I	Class II	Class III: Fresh	Class III: Marine	Class IV	Class V
—	(28) 1,1-Dichloroethylene (1,1-dichloroethene)	Micrograms/L	≤ 0.057 annual avg.; ≤ 7.0 max	≤ 3.2 annual avg.	≤ 3.2 annual avg.	≤ 3.2 annual avg.		
--	(29) Dichloromethane (methylene chloride)	Micrograms/L	≤ 4.65 annual avg.	≤ 1,580 annual avg.	≤ 1,580 annual avg.	≤ 1,580 annual avg.		
--	(30) 2,4-Dinitrotoluene	Micrograms/L	≤ 0.11 annual avg.	≤ 9.1 annual avg.	≤ 9.1 annual avg.	≤ 9.1 annual avg.		
6 – 7 [illegible]	(31) Dissolved Oxygen	Milligrams/L	Shall not be less than 5.0. Normal daily and seasonal fluctuations above this level shall be maintained.	Shall not average less than 5.0 in a 24-hour period and shall never be less than 4.0. Normal daily and seasonal fluctuations above these levels shall be maintained.	Shall not be less than 5.0. Normal daily and seasonal fluctuations above these levels shall be maintained.	Shall not average less than 5.0 in a 24-hour period and shall never be less than 4.0. Normal daily and seasonal fluctuations above these levels shall be maintained.	Shall not average less than 4.0 in a 24-hour period and shall never be less than 3.0.	Shall not be less than 0.3, fifty percent of the time on an annual basis for flows greater than or equal to 250 cubic feet per second and shall never be less than 0.1. Normal daily and seasonal fluctuations above these levels shall be maintained.
500-1000	(32) Dissolved Solids	Milligrams/L	≤ 500 as a monthly avg.; ≤ 1,000 max					
1 – 1.5	(33) Fluorides	Milligrams/L	≤ 1.5	≤ 1.5	≤ 10.0	≤ 5.0	≤ 10.0	≤ 10.0
—	(34) "Free Froms" (see Minimum Criteria in Section 17-302.500, F.A.C.)							
—	(35) "General Criteria" (see Section 17-302.510, F.A.C. and individual criteria)							

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "ln H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

ORG N 1.5 - [illegible] mg/L
N-NH$_4^+$ 0.5 - 2.5 mg/L
N-NO$_2^-$ 0.02-0.05 mg/L
N-NO$_3$ 3.4 - 11 mg/L

TOTAL PHOSPHORUS
0.15 - 0

Parameter	Units	Class I	Class II	Class III: Fresh	Class III: Marine	Class IV	Class V
(48) (a) Nutrients		The discharge of nutrients shall continue to be limited as needed to prevent violations of other standards contained in this chapter. Man-induced nutrient enrichment (total nitrogen or total phosphorus) shall be considered degradation in relation to the provisions of Sections 17-302.300, 17-302.700, and 17-4.242, F.A.C.					
(48) (b) Nutrients		In no case shall nutrient concentrations of a body of water be altered so as to cause an imbalance in natural populations of aquatic flora or fauna.					
(49) Odor (also see Color, Minimum Criteria, Phenolic Compounds, etc.)	Threshold odor number		Shall not exceed 24 at 60 degrees C as a daily average.				Odor producing substances: only in such amounts as will not unreasonably interfere with use of the water for the designated purpose of this classification.
(50) (a) Oils and Greases	Milligrams/L	Dissolved or emulsified oils and greases shall not exceed 5.0	Dissolved or emulsified oils and greases shall not exceed 5.0	Dissolved or emulsified oils and greases shall not exceed 5.0	Dissolved or emulsified oils and greases shall not exceed 5.0	Dissolved or emulsified oils and greases shall not exceed 5.0	Dissolved or emulsified oils and greases shall not exceed 10.0
(50) (b) Oils and Greases		No undissolved oil, or visible oil defined as iridescence, shall be present so as to cause taste or odor, or otherwise interfere with the beneficial use of waters.					
(51) Pesticides and Herbicides							
(51) (a) 2,4,5-TP	Micrograms/L	≤ 10					
(51) (b) 2-4-D	Micrograms/L	≤ 100					
(51) (c) Aldrin	Micrograms/L	≤ .00013 annual avg.; 3.0 max	≤ .00014 annual avg.; 1.3 max	≤ .00014 annual avg.; 3.0 max	≤ .00014 annual avg.; 1.3 max		
(51) (d) Beta-hexachlorocyclohexane (b-BHC)	Micrograms/L	≤ 0.014 annual avg.	≤ 0.046 annual avg.	≤ 0.046 annual avg.	≤ 0.046 annual avg.		

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "In H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

	Parameter	Units	Class I	Class II	Class III: Fresh	Class III: Marine	Class IV	Class V
—	(36) (b) 5. Halomethanes (individual): Dichlorobromomethane	Micrograms/L	$\leq$0.27 annual avg.	$\leq$22 annual avg.	$\leq$22 annual avg.	$\leq$22 annual avg.		
-	(37) Hexachlorobutadiene	Micrograms/L	$\leq$0.45 annual avg.	$\leq$49.7 annual avg.	$\leq$49.7 annual avg.	$\leq$49.7 annual avg.		
—	(38) Imbalance (see Nutrients)							
—	(39) Iron	Milligrams/L	$\leq$0.3	$\leq$0.3	$\leq$1.0	$\leq$0.3	$\leq$1.0	
50-100	(40) Lead	Micrograms/L	$Pb \leq e^{(1.273[\ln H]-4.705)}$; 50 max	$\leq$5.6	$Pb \leq e^{(1.273[\ln H]-4.705)}$; 50 max	$\leq$5.6	$\leq$50	$\leq$50
—	(41) Manganese	Milligrams/L		$\leq$0.1				
0.5-1.0	(42) Mercury	Micrograms/L	$\leq$0.012	$\leq$0.025	$\leq$0.012	$\leq$0.025	$\leq$0.2	$\leq$0.2
	(43) Minimum Criteria (see Section 17-302. 500, F.A.C.)							
	(44) Mixing Zones (See Section 17-4.246, F.A.C.)							
50-150	(45) Nickel	Micrograms/L	$Ni \leq e^{(0.846[\ln H]+1.1645)}$	$\leq$8.3	$Ni \leq e^{(0.846[\ln H]+1.1645)}$	$\leq$8.3	$\leq$100	
3.4-11	(46) Nitrate	Milligrams/L as N	$\leq$10 or that concentration that exceeds the nutrient criteria					
	(47) Nuisance Species		Substances in concentrations which result in the dominance of nuisance species: none shall be present.					

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "In H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

Parameter	Units	Class I	Class II	Class III: Fresh	Class III: Marine	Class IV	Class V
(52) (b) pH (Class II Waters)	Standard Units	Shall not vary more than one unit above or below natural background of coastal waters as defined in Section 17-302.520(3)(b), F.A.C., or more than two-tenths unit above or below natural background of open waters as defined in Section 17-302.520(3)(f), F.A.C., provided that the pH is not lowered to less than 6.5 units or raised above 8.5 units. If natural background is less than 6.5 units, the pH shall not vary below natural background or vary more than one unit above natural background for coastal waters or more than two-tenths unit above natural background for open waters. If natural background is higher than 8.5 units, the pH shall not vary above natural background or vary more than one unit below natural background of coastal waters or more than two-tenths unit below natural background of open waters.					
(52) (c) pH (Class III Waters)	Standard Units	Shall not vary more than one unit above or below natural background of predominantly fresh waters and coastal waters as defined in Section 17-302.520(3)(b), F.A.C. or more than two-tenths unit above or below natural background of open waters as defined in Section 17-302.520(3)(f), F.A.C., provided that the pH is not lowered to less than 6 units in predominantly fresh waters, or less than 6.5 units in predominantly marine waters, or raised above 8.5 units. If natural background is less than 6 units, in predominantly fresh waters or 6.5 units in predominantly marine waters, the pH shall not vary below natural background or vary more than one unit above natural background of predominantly fresh waters and coastal waters, or more than two-tenths unit above natural background of open waters. If natural background is higher than 8.5 units, the pH shall not vary above natural background or vary more than one unit below natural background of predominantly fresh waters and coastal waters, or more than two-tenths unit below natural background of open waters.					
(52) (d) pH (Class V Waters)	Standard Units	Not lower than 5.0 nor greater than 9.5 except certain swamp waters which may be as low as 4.5.					
(53) (a) Phenolic Compounds: Total (Class I, Class II, Class III, and Class IV)	Micrograms/L	1. Phenolic compounds as listed - Total chlorinated phenols, including trichlorophenols, and chlorinated cresols, shall not exceed 1.0 except as set forth in (b) 1. to (b) 6. below or unless higher values are shown not to be chronically toxic. Such higher values shall be approved in writing by the Secretary. In addition, the compounds listed below shall not exceed the limits specified for each compound. Phenolic compounds other than those produced by the natural decay of plant material, listed or unlisted, shall not taint the flesh of edible fish or shellfish or produce objectionable taste or odor in a drinking water supply.					
(53) (b) 1. Phenolic Compound: 2-chlorophenol	Micrograms/L	≤ 120	≤ 400	≤ 400	≤ 400	≤ 400	
(53) (b) 2. Phenolic Compound: 2,4-dichlorophenol	Micrograms/L	≤ 93	≤ 790	≤ 790	≤ 790	≤ 790	
(53) (b) 3. Phenolic Compound: 2,4-dinitrophenol	Milligrams/L	≤ 0.0697	≤ 14.26	≤ 14.26	≤ 14.26	≤ 14.26	

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "In H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

Parameter	Units	Class I	Class II	Class III: Fresh	Class III: Marine	Class IV	Class V
(51) (e) Chlordane	Micrograms/L	≤0.00058 annual avg.; 0.0043 max	≤0.00059 annual avg.; 0.004 max	≤0.00059 annual avg.; 0.0043 max	≤0.00059 annual avg.; 0.004 max		
(51) (f) DDT	Micrograms/L	≤0.00059 annual avg.; 0.001 max	≤0.00059 annual avg.; 0.001 max	≤0.00059 annual avg.; 0.001 max	≤0.00059 annual avg.; 0.001 max		
(51) (g) Demeton	Micrograms/L	≤0.1	≤0.1	≤0.1	≤0.1		
(51) (h) Dieldrin	Micrograms/L	≤0.00014 annual avg.; 0.0019 max	≤0.00014 annual avg.; 0.0019 max	≤0.00014 annual avg.; 0.0019 max	≤0.00014 annual avg.; 0.0019 max		
(51) (i) Endosulfan	Micrograms/L	≤0.056	≤0.0087	≤0.056	≤0.0087		
(51) (j) Endrin	Micrograms/L	≤0.0023	≤0.0023	≤0.0023	≤0.0023		
(51) (k) Guthion	Micrograms/L	≤0.01	≤0.01	≤0.01	≤0.01		
(51) (l) Heptachlor	Micrograms/L	≤0.00021 annual avg.; 0.0038 max	≤0.00021 annual avg.; 0.0036 max	≤0.00021 annual avg.; 0.0038 max	≤0.00021 annual avg.; 0.0036 max		
(51) (m) Lindane (g-benzene hexachloride)	Micrograms/L	≤0.019 annual avg.; 0.08 max	≤0.063 annual avg.; 0.16 max	≤0.063 annual avg.; 0.08 max	≤0.063. annual avg.; 0.16 max		
(51) (n) Malathion	Micrograms/L	≤0.1	≤0.1	≤0.1	≤0.1		
(51) (o) Methoxychlor	Micrograms/L	≤0.03	≤0.03	≤0.03	≤0.03		
(51) (p) Mirex	Micrograms/L	≤0.001	≤0.001	≤0.001	≤0.001		
(51) (q) Parathion	Micrograms/L	≤0.04	≤0.04	≤0.04	≤0.04		
(51) (r) Toxaphene	Micrograms/L	≤0.0002	≤0.0002	≤0.0002	≤0.0002		
(52) (a) pH (Class I and Class IV Waters)	Standard Units	Shall not vary more than one unit above or below natural background provided that the pH is not lowered to less than 6 units or raised above 8.5 units. If natural background is less than 6 units, the pH shall not vary below natural background or vary more than one unit above natural background. If natural background is higher than 8.5 units, the pH shall not vary above natural background or vary more than one unit below background.					

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "ln H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

ND — 25000

Parameter	Units	Class I	Class II	Class III: Fresh	Class III: Marine	Class IV	Class V
(55) Phthalate Esters	Micrograms/L	≤ 3.0		≤ 3.0			
(56) Polychlorinated Biphenyls (PCBs)	Micrograms/L	≤ 0.000044 annual avg.; 0.014 max	≤ 0.000045 annual avg.; 0.03 max	≤ 0.000045 annual avg.; 0.014 max	≤ 0.000045 annual avg.; 0.03 max		
(57) (a) Polycyclic Aromatic Hydrocarbons (PAHs). Total of: Acenaphthylene; Benzo(a)anthracene; Benzo(a)pyrene; Benzo(b)fluoranthene; Benzo(ghi)perylene; Benzo(k)fluoranthene; Chrysene; Dibenzo-(a,h)anthracene; Indeno(1,2,3-cd)pyrene; and Phenanthrene	Micrograms/L	≤ 0.0028 annual avg.	≤ 0.031 annual avg.	≤ 0.031annual avg.	≤ 0.031 annual avg.		
(57) (b) 1. (Individual PAHs): Anthracene	Milligrams/L	≤ 9.6	≤ 110	≤ 110	≤ 110		
(57) (b) 2. (Individual PAHs): Fluorene	Milligrams/L	≤ 1.3	≤ 14	≤ 14	≤ 14		
(57) (b) 3. (Individual PAHs): Pyrene	Milligrams/L	≤ 0.96	≤ 11	≤ 11	≤ 11		
(57) (b) 4. (Individual PAHs): Fluoranthene	Milligrams/L	≤ 0.3	≤ 0.370	≤ 0.370	≤ 0.370		
(57) (b) 5. (Individual PAHs): Acenaphthene	Milligrams/L	≤ 1.2	≤ 2.7	≤ 2.7	≤ 2.7		

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "ln H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

Parameter	Units	Class I	Class II	Class III: Fresh	Class III: Marine	Class IV	Class V
(53) (b) 4. Phenolic Compound: 2,4,6-trichlorophenol	Micrograms/L	≤ 2.1 annual avg.	≤ 6.5 annual avg.	≤ 6.5 annual avg.	≤ 6.5 annual avg.	≤ 6.5 annual avg.	
(53) (b) 5. Phenolic Compound: Penta-chlorophenol	Micrograms/L	≤ 30 max; ≤ 0.28 annual avg; $\leq e^{(1.005[pH]-5.29)}$	≤ 7.9	≤ 30 max; ≤ 8.2 annual avg; $\leq e^{(1.005[pH]-5.29)}$	≤ 7.9	≤ 30	
(53) (b) 6. Phenolic Compound: Phenol	Milligrams/L	≤ 21	≤ 4,600	≤ 4,600	≤ 4,600	≤ 4,600	
(53) (c) Phenolic Compounds: Total (Class V)	Milligrams/L						Phenolic compounds as listed: Chlorinated phenols, including trichlorophenols; chlorinated cresols; 2-chlorophenol; 2,4-di-chlorophenol; pentachlorophenol; and 2,4-dinitrophenol, shall not exceed 0.05. Phenol: shall not exceed 0.2. Phenolic compounds other than those produced by the natural decay of plant material, listed or unlisted, shall not taint the flesh of edible fish or shellfish.
(54) Phosphorus (Elemental)	Micrograms/L		≤ 0.1		≤ 0.1		

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "In H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

Parameter	Units	Class I	Class II	Class III: Fresh	Class III: Marine	Class IV	Class V
(66) Thermal Criteria (See Section 17-302.520)							
(67) Total Dissolved Gases	Percent of the saturation value for gases at the existing atmospheric and hydrostatic pressures	≤ 110% of saturation value	≤ 110% of saturation value	≤ 110% of saturation value	≤ 110% of saturation value		
(68) Transparency	Depth of the compensation point for photosynthetic activity	Shall not be reduced by more than 10% as compared to the natural background value.	Shall not be reduced by more than 10% as compared to the natural background value.	Shall not be reduced by more than 10% as compared to the natural background value.	Shall not be reduced by more than 10% as compared to the natural background value.		
(69) Trichloroethylene (trichloroethene)	Micrograms/L	≤ 2.7 annual avg., ≤ 3.0 max	≤ 80.7 annual avg.	≤ 80.7 annual avg.	≤ 80.7 annual avg.		
(70) 1,1,1-Trichloroethane	Milligrams/L	≤ 3.100	≤ 173	≤ 173	≤ 173		
(71) Turbidity	Nephelometric Turbidity Units (NTU)	≤ 29 above natural background conditions	≤ 29 above natural background conditions	≤ 29 above natural background conditions	≤ 29 above natural background conditions	≤ 29 above natural background conditions	≤ 29 above natural background conditions
(72) Zinc	Micrograms/L	$Zn \le e^{(0.8473[\ln H]+0.7614)}$; ≤ 1,000	≤ 86	$Zn \le e^{(0.8473[\ln H]+0.7614)}$; ≤ 1,000	≤ 86	≤ 1,000	≤ 1,000

50-2[illegible]

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "ln H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

	Parameter	Units	Class I	Class II	Class III: Fresh	Class III: Marine	Class IV	Class V
1-.3 Eq/L	(58) (a) Radioactive substances (Combined radium 226 and 228)	Picocuries/L	≤ 5	≤ 5	≤ 5	≤ 5	≤ 5	≤ 5
	(58) (b) Radioactive substances (Gross alpha particle activity including radium 226, but excluding radon and uranium)	Picocuries/L	≤ 15	≤ 15	≤ 15	≤ 15	≤ 15	≤ 15
10-50	(59) Selenium	Micrograms/L	≤ 5.0	≤ 71	≤ 5.0	≤ 71		
10-50	(60) Silver	Micrograms/L	≤ 0.07	≤ 0.05	≤ 0.07	≤ 0.05		
—	(61) Specific Conductance (see Conductance, Specific, above)							
—	(62) Substances in concentrations which injure, are chronically toxic to, or produce adverse physiological or behavioral response in humans, plants, or animals		None shall be present.					
—	(63) 1,1,2,2-Tetrachloroethane	Micrograms/L	≤ 0.17 annual avg.	≤ 10.8 annual avg.	≤ 10.8 annual avg.	≤ 10.8 annual avg.		
—	(64) Tetrachloroethylene (1,1,2,2-tetrachloroethene)	Micrograms/L	≤ 0 8 annual avg., ≤ 3.0 max	≤ 8.85 annual avg.	≤ 8.85 annual avg.	≤ 8.85 annual avg.		
—	(65) Thallium	Micrograms/L	≤ 13	≤ 48	≤ 48	≤ 48		

Notes: (1) "Annual avg." means the maximum concentration at average annual flow conditions (see Section 17-4.020(1), F.A.C.); (2) "Max" means the maximum not to be exceeded at any time; (3) "In H" means the natural logarithm of total hardness expressed as milligrams/L of $CaCO_3$.

Indices III

(Indicators of amounts of substances in surface waters)

Index	Symbol	Unit	Value for water-works water courses	Value for other surface waters[1)]
1	2	3	4	5
1. Dissolved oxygen	O_2	mg/l	min. 6	min. 4
2. Biochemical oxygen demand	BOD_5	mg/l	4	8
3. Chemical oxygen demand - permanganate	COD_{Mn}	mg/l	8	20
4. Chemical oxygen demand - dichromate	COD_{Cr}	mg/l	20	50
5. Sulfane (H_2S) and sulfides	S^{2-}	mg/l	PMC[2)]	0.02
6. Water reaction	pH	6.0 - 8.0		6.0 - 9.0
7. Soluble substances	SS	mg/l	500	1 000
8. Total iron	Fe	mg/l	0.5	2.0
9. Total manganese	Mn	mg/l	0.2	0.5
10. Ammoniacal nitrogen	$N\text{-}NH_4^+$	mg/l	0.5	2.5
11. Free ammonia	NH_3	mg/l	PMC	0.5
12. Nitrite nitrogen	$N\text{-}NO_2^-$	mg/l	0.02	0.05
13. Nitrate nitrogen	$N\text{-}NO_3^-$	mg/l	3.4	11
14. Organic nitrogen	N-org	mg/l	1.5	3.0
15. Total phosphorus	P	mg/l	0.15	0.4
16. Chlorides	Cl^-	mg/l	150	350
17. Sulfates	SO_4^{2-}	mg/l	200	300
18. Calcium	Ca	mg/l	200	300
19. Magnesium	Mg	mg/l	100	200
20. Fluorides	F^-	mg/l	1.0	1.5
21. Phenols vaporized with water vapour	FN1	mg/l	0.02	0.1
22. Anionic tensides	PAL-A	mg/l	0.2	1.0
23. Nonpolar extractable substances	NES	mg/l	0.05	0.2
24. Total cyanide	CN^-	mg/l	PMC	0.2
25. Active chlorine	Cl_2	mg/l	PMC	0.05
26. Extractable organically bonded chlorine	EOCl	mg/l	0.01	0.025
27. Boron	B	mg/l	0.3	0.5
28. Mercury	Hg	mg/l	0.0005	0.001
29. Cadmium	Cd	mg/l	0.005	0.015
30. Lead	Pb	mg/l	0.05	0.1
31. Arsenic	As	mg/l	0.05	0.1
32. Copper	Cu	mg/l	0.05	0.1
33. Total chromium	Cr	mg/l	0.1	0.3
34. Chromium (VI)	Cr^{VI}	mg/l	0.02	0.05
35. Cobalt	Co	mg/l	0.05	0.1
36. Nickel	Ni	mg/l	0.05	0.15
37. Zinc	Zn	mg/l	0.05	0.2
38. Vanadium	V	mg/l	0.02	0.1
39. Silver	Ag	mg/l	0.01	0.05
40. Selenium	Se	mg/l	0.01	0.05
41. Barium	Ba	mg/l	1.0	2.0
42. Beryllium	Be	mg/l	0.0002	0.001
43. Total volume alpha activity	Aa	Bq/l	0.3	0.5
44. Total volume beta activity	Ab	Bq/l	1.0	2.0
45. Radium 226	Ra226	Bq/l	0.1	0.3
46. Uranium	U	mg/l	0.05	0.1

Indices III (cont.)

(Indicators of amounts of substances in surface waters)

Index	Symbol	Unit	Value for water-works water courses	Value for other surface waters[1)]
1	2	3	4	5
47. Tritium	H3(T)	Bq/l	700	5 000
48. Strontium 90 and yttrium 90	Sr 90 + Y 90	Bq/l		0.305
49. Cesium	Cs137	Bq/l	0.5	1.0
50. Coliform bacteria	Coli	KTJ/l[3)]	20 000	200 000
51. Faecal coliform bacteria	Fecoli	KTJ/l	4 000	40 000
52. Enterococci	Enco	KTJ/l	2 000	20 000
53. Benzene	BZ	mg/l	0.01	0.05
54. Chlorobenzene	CB	mg/l	0.003	0.01
55. Dichlorobenzenes	DCB	mg/l	0.0003	0.001
56. Polychlorinated biphenyls	PCB	mg/l	PMC	25
57. Benzo(a)pyrene	BZP	mg/l	10	50

Note:

[1)] Except for the index "dissolved oxygen", these are maximum permissable values

[2)] PMC - below the detection limit

[3)] KTJ - unit-forming colonies

[4)] Limiting concentrations of toxic substances are related to the sum of dissolved and undissolved forms of the individual substances

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AMMONIA

QUALITY CRITERIA FOR WATER

CRITERION

0.02 mg/l (as un-ionized ammonia) for freshwater aquatic life.

Table 2.—Concentrations of total ammonia (NH_3 + NH_4^+) which contain an un-ionized ammonia concentration of 0.020 mg/l NH_3(mg/l)*

Temperature (°C)	pH Value								
	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
5....	160.	51.	16.	5.1	1.6	0.53	0.18	0.071	0.036
10....	110.	34.	11.	3.4	1.1	0.36	0.13	0.054	0.031
15....	73.	23.	7.3	2.3	0.75	0.25	0.093	0.043	0.027
20....	50.	16.	5.1	1.6	0.52	0.18	0.070	0.036	0.025
25....	35.	11.	3.5	1.1	0.37	0.13	0.055	0.031	0.024
30....	25.	7.9	2.5	0.81	0.27	0.099	0.045	0.028	0.022

*[Abstracted from Thurston et al. (1974)]

INTRODUCTION

Ammonia is a pungent, colorless, gaseous, alkaline compound of nitrogen and hydrogen that is highly soluble in water. It is a biologically active compound present in most waters as a normal biological degradation product of nitrogenous organic matter. It may also reach ground and surface waters through discharge of industrial wastes containing ammonia as a byproduct, or wastes from industrial processes using "ammonia water."

When ammonia dissolves in water, some of the ammonia reacts with the water to form ammonium ions. A chemical equilibrium is established which contains un-ionized ammonia (NH_3), ionized ammonia (NH_4^+), and hydroxide ions (OH^-). The equilibrium for these chemical species can be expressed in simplified form by the following equation:

$$NH_3 + H_2O = NH_3 \cdot H_2O = NH_4^+ + OH^-$$

In the above equation, NH_3 represents ammonia gas combining with water. The term $NH_3 \cdot H_2O$ represents the un-ionized ammonia molecule which is loosely attached to water molecules. Dissolved un-ionized ammonia will be represented for convenience as NH_3. The ionized form of ammonia will be represnted as NH_4^+. The term total ammonia will refer to the sum of these (NH_3 + NH_4^+).

The toxicity of aqueous solutions of ammonia is attributed to the NH_3 species. Because of the equilibrium relationship among NH_3, NH_4^+, and OH^-, the toxicity of ammonia is very much dependent upon pH as well as the concentration of total ammonia. Other factors a[illegible] affect the concentration of NH_3 in water solutions, the most important of which are temperature and ionic strength. The concentration of NH_3 increases with increasing temperature, and decreases with increasing ionic strength. In aqueous ammonia solutions of dilute saline concentrations, the NH_3 concentration decreases with increasing salinity.

Percent NH_3 for aqueous ammonia solutions of zero salinity at different values of pH and temperature is given in Table 3. This percentage can be used to determine the amount of total ammonia which is in the most toxic (NH_3) form.

Table 3.—Percent un-ionized ammonia in aqueous ammonia solutions*

Temperature (°C)	pH Value								
	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
5....	0.013	0.040	0.12	0.39	1.2	3.8	11.	28.	56.
10....	0.019	0.059	0.19	0.59	1.8	5.6	16.	37.	65.
15....	0.027	0.087	0.27	0.86	2.7	8.0	21.	46.	73.
20....	0.040	0.13	0.40	1.2	3.8	11.	28.	56.	80.
25....	0.057	0.18	0.57	1.8	5.4	15.	36.	64.	85.
30....	0.080	0.25	0.80	2.5	7.5	20.	45.	72.	89.

*[Thurston, et al. (1974)]

RATIONALE

It has been known since early in this century that ammonia is toxic to fishes and that the toxicity varies with the pH of the water. Chipman (1934) demonstrated that undissociated ammonia (NH_3) was the chemical species toxic to goldfish, amphipods, and cladocerans. He concluded from his studies that the toxicity of ammonium salts was pH-dependent and was directly related to the concentration of undissociated ammonia. Chipman's work was confirmed by Wuhrmann, et al. (1947) who concluded that the NH_3 fraction was toxic to fish and that the NH_4^+ fraction had little or no toxicity. Further studies by Wuhrmann and Woker (1948) and Downing and Merkens (1955) agreed with these earlier findings. Tabata (1962), however, has attributed some degree of toxicity to fishes and invertebrates by the NH_4^+ species (less than 1/50th that of NH_3).

In most natural waters, the pH range is such that the NH_4^+ fraction of ammonia predominates; however, in highly alkaline waters, the NH_3 fraction can reach toxic levels. Many laboratory experiments of relatively short duration have demonstrated that the lethal concentrations for a variety of fish species are in the range of 0.2 to 2.0 mg/l NH_3, with trout being the most sensitive and carp the most resistant. Although coarse fish such as carp survive longer in toxic solutions than do salmonids, the difference in sensitivity among fish species to prolonged exposure is probably small (European Inland Fisheries Advisory Commission, 1970). The lowest lethal concentration reported for salmonids is 0.2 mg/l NH_3 for rainbow trout fry, *Salmo gairdneri*

ATTACHMENT C

(Liebmann, 1960). The toxic concentration for Atlantic salmon smolts, *Salmo salar* (Herbert and Shurben, 1965), and for rainbow trout (Ball, 1967) was found to be only slightly higher. Although a concentration of NH_3 below 0.2 mg/l may not kill a significant proportion of a fish population, such concentration may still exert an adverse physiological or histopathological effect (Flis, 1968; Lloyd and Orr, 1969; Smith and Piper, 1975). Fromm (1970) found that at concentrations of 3 mg/l ammonia as N, the trout became hyperexcitable; at 5 mg/l, ammonia excretion by rainbow trout was inhibited; and at 8 mg/l, 50 percent died within 24 hours. Burrows (1964) found progressive gill hyperplasia in fingerling chinook salmon, *Oncorhynchus tshawytscha*, during a 6-week exposure to a total ammonia concentration (expressed as NH_4) of 0.3 mg/l (0.002 mg/l NH_3), which was the lowest concentration applied. Reichenbach-Klinke (1967) also noted gill hyperplasia, as well as pathological effects on the liver and blood of various species at a concentration of 0.27 mg/l NH_3. Flis (1968) noted that exposure of carp, *Cyprinus carpio*, to sublethal NH_3 concentrations resulted in extensive necrotic changes and tissue disintegration in various organs.

Herbert and Shurben (1965) reported that the resistance of yearling rainbow trout to ammonia increased with salinity (i.e., dilution with about 30 percent seawater) but above that level resistance appeared to decrease. Katz and Pierro (1967) subjected fingerling coho salmon, *Oncorhynchus kisutch*, to an ammonia waste at salinity levels of 20, 25, and 29 parts per thousand (i.e., dilution with about 57–83 percent seawater) and also found that toxicity increased with increased salinity. In saline waters the NH_4^+/NH_3 ratio must be adjusted by consideration of the activity of the charged species and total ionic strength of the solution. In dilute saline waters this ratio will change to favor NH_4^+, and thereby reduce the concentration of the toxic NH_3 species. At higher salinity levels the reported toxic effects of ammonia to fish must therefore be attributed to some mechanism other than changes in the NH_4^+/NH_3 ratio. Data on the effect of ammonia on marine species are limited and the information on anadromous species generally has been reported in conjunction with studies on freshwater species.

Although the NH_3 fraction of total ammonia increases with temperature, the toxic effect of NH_3 versus temperature is not clear. Burrows (1964) has reported that the recovery rate from hyperplasia in gill tissues of chinook salmon, *Oncorhynchus tshawytscha*, exposed first to ammonia at sublethal levels and then to fresh water was less at 6°C than at 14°C. In this experiment, comparison was made between two different age classes of salmon.

Levels of un-ionized ammonia in the range of 0.20 to 2 mg/l have been shown to be toxic to some species of freshwater aquatic life. To provide safety for those life forms not examined, 1/10th of the lower value of this toxic effect range results in a criterion of 0.020 mg/l of un-ionized ammonia. This criterion is slightly lower than that recommended for European inland fisheries (EIFAC, 1970) for temperatures above 5°C and pH values below 8.5. Measurement of values of total ammonia for calculation of values in the range of 0.020 mg/l NH_3 is well within curr[illegible]nalytical capability.

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(B) Rinse process equipment with an appropriate solvent until dioxins and dibenzofurans are not detected in the final solvent rinse.

(iii) Analytical requirements.

(A) Rinses must be tested in accordance with SW-846, Method 8290.

(B) "Not detected" means at or below the lower method calibration limit (MCL) in Method 8290, Table 1.

(iv) The generator must manage all residues from the cleaning process as F032 waste.

(3) Replacement requirements.

(i) Prepare and sign a written equipment replacement plan that describes:

(A) The equipment to be replaced;

(B) How the equipment will be replaced; and

(C) How the equipment will be disposed.

(ii) The generator must manage the discarded equipment as F032 waste.

(4) Documentation requirements.

(i) Document that previous equipment cleaning and/or replacement was performed in accordance with this section and occurred after cessation of use of chlorophenolic preservatives.

(c) The generator must maintain the following records documenting the cleaning and replacement as part of the facility's operating record:

(1) The name and address of the facility;

(2) Formulations previously used and the date on which their use ceased in each process at the plant;

(3) Formulations currently used in each process at the plant;

(4) The equipment cleaning or replacement plan;

(5) The name and address of any persons who conducted the cleaning and replacement;

(6) The dates on which cleaning and replacement were accomplished;

(7) The dates of sampling and testing;

(8) A description of the sample handling and preparation techniques, including techniques used for extraction, containerization, preservation, and chain-of-custody of the samples;

(9) A description of the tests performed, the date the tests were performed, and the results of the tests;

(10) The name and model numbers of the instrument(s) used in performing the tests;

(11) QA/QC documentation; and

(12) The following statement signed by the generator or his authorized representative:

I certify under penalty of law that all process equipment required to be cleaned or replaced under 40 CFR 261.35 was cleaned or replaced as represented in the equipment cleaning and replacement plan and accompanying documentation. I am aware that there are significant penalties for providing false information, including the possibility of fine or imprisonment.

EFFECTIVE DATE NOTE: At 55 FR 50482, Dec. 6, 1990, §261.35 was added. Paragraph (c) contains information collection and recordkeeping requirements and will not become effective until approval has been given by the Office of Management and Budget. A notice will be published in the FEDERAL REGISTER once approval has been obtained.

APPENDICES TO PART 261

APPENDIX I— REPRESENTATIVE SAMPLING METHODS

The methods and equipment used for sampling waste materials will vary with the form and consistency of the waste materials to be sampled. Samples collected using the sampling protocols listed below, for sampling waste with properties similar to the indicated materials, will be considered by the Agency to be representative of the waste.

Extremely viscous liquid—ASTM Standard D140-70 Crushed or powdered material—ASTM Standard D346-75 Soil or rock-like material—ASTM Standard D420-69 Soil-like material—ASTM Standard D1452-65

Fly Ash-like material—ASTM Standard D2234-76 [ASTM Standards are available from ASTM, 1916 Race St., Philadelphia, PA 19103]

Containerized liquid wastes-"COLIWASA" described in "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods," [1a]U.S., Environmental Protection Agency, Office of Solid Waste, Washington, D.C. 20460. [Copies may be obtained from Solid Waste Information, U.S. Environmental Protection Agency, 26 W. St. Clair St., Cincinnati, Ohio 45268]

Liquid waste in pits, ponds, lagoons, and similar reservoirs.—"Pond Sampler" described in "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods."[1a]

This manual also contains additional information on application of these protocols.

APPENDIX II—METHOD 1311 TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)

1.0 Scope and Application

1.1 The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.2 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

1.3 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be equal to or above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte equals or exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.0 Summary of Method

2.1 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 μm glass fiber filter, is defined as the TCLP extract.

2.2. For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20

[1a] These methods are also described in "Samplers and Sampling Procedures for Hazardous Waste Streams," EPA 600/2-80-018, January 1980.

times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 Interferences

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 Apparatus and Materials

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ±2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessels.

4.2.1 Zero-Headspace Extraction Vessel (ZHE). This device is for use only when the waste is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see section 4.3.1). The vessels shall have an internal volume of 500-600 mL, and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.[1]

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 pounds per square inch (psi) or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedures (see section 7.3) refers to pounds per square inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

4.2.2 Bottle Extraction Vessel. When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see section 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in section 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extractor Vessel (ZHE): When the waste is evaluated for volatiles, the zero-headspace extraction vessel described in section 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see section 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10%) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 mm, or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 L per rinse is recommended). Glass fiber filter are fragile and should be handled with care.

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[1] VITON® is a registered trademark of DuPont.

4.5 pH Meters: The meter should be accurate to ±0.05 units at 25°C.

4.6 ZHE Extract Collection Devices: TEDLAR®[2] bags or glass, stainless steel or PTFE gag-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions:[2]

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1% of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1% of total waste), the syringe or the TEDLAR® bag may be used for both the intitial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100% solid) or has no significant solid phase (is 100% liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g, a positive displacement or peristaltic pump, a gas tight syringe, pressure filtration unit (see section 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ±0.01 grams may be used (all weight measurements are to be within ±0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

4.10 Watchglass, appropriate diameter to cover beaker or erlenmeyer flask.

4.11 Magnetic stirrer.

5.0 Reagents

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. Reagent water is defined as water in which an interferant is not observed at or above the methods detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.2.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.2.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 + 5 degrees C, bubble a contaminant-free inert gas (e.g., nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.3 Hydrochloric acid (1N), HCl, made from ACS reagent grade.

5.4 Nitric acid (1N), HNO_3, made from ACS reagent grade.

5.5 Sodium hydroxide (1N), NaOH, made from ACS reagent grade.

5.6 Clacial acetic acid, CH_3CH_2OOH, ACS reagent grade.

5.7 Extraction fluid.

5.7.1 Extraction fluid #1: Add 5.7 mL glacial CH_3CH_2OOH to 500 mL of reagent water (See section 5.2), add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93±0.05.

5.7.2 Extraction fluid #2: Dilute 5.7 mL glacial CH_3CH_2OOH with reagent water (See section 5.2) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88±0.05.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.8 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 The TCLP may place requirements on the minimal size of the field sample, depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure. Another aliquot may be needed to actually conduct the nonvolatile extraction (see section 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more samples just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the waste is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4 °C. Samples should be opened only immediately prior to extraction).

6.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH <2, unless precipitation occurs (see section 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See section 8.0 (QA requirements)

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[2] TEDLAR® is a registered trademark of Dupont.

for acceptable sample and extract holding times.

7.0 Procedure

7.1 Preliminary Evaluations. Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) Determination of the percent solids (section 7.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (section 7.1.2); (3) determination of whether the solid portion of the waste requires particle size reduction (section 7.1.3); and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste (section 7.1.4.).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to section 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in section 4.3.2 and is outlined in sections 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in section 7.1.1.5 to determine he weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in section 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see section 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in section 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (section 7.1.1.9)}}{\text{Total weight of waste (section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in section 7.1.1.9 is equal to or greater than 0.5%, then proceed either to section 7.1.3 to determine whether the solid material requires particle size reduction or to section 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in section 7.1.1.9 is less than 0.5%, then proceed to section 7.2.9 if the nonvolatile TCLP is to be performed and to section 7.3 with a fresh portion of the waste if the volatile TCLP is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100±20°C until two successive weighings yield the same value within ±1%. Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{\% dry solids} = \frac{\text{(Weight of dry waste+filter)-tared weight of filter}}{\text{Initial weight of waste (section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to section 7.2.9 if the nonvolatile TCLP is to be performed, and to section 7.3 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this section (7.1) and, with a fresh portion of waste, determine whether particle size reduction is necessary (section 7.1.3) and determine the appropriate extraction fluid (section 7.1.4). If only the volatile TCLP is to be performed, see the note in section 7.1.4.

7.1.3 Determination of whether the waste requires particle size reduction (particle size is reduced during this step): Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see section 7.3.6).

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid: If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for nonvolatile constituents (section 7.2), determine the appropriate fluid (section 5.7) for the nonvolatiles extraction as follows:

NOTE: TCLP extraction for volatile constituents uses only extraction fluid #1 (section 5.7.1). Therefore, if TCLP extraction for nonvolatiles is not required, proceed to section 7.3.

7.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.

7.1.4.2 Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to section 7.2.

7.1.4.3 If the pH from section 7.1.4.2 is >5.0, add 3.5 mL 1N NCl, slurry briefly, cover with a watchglass, heat to 50°C, and hold at 50°C for 10 minutes.

7.1.4.4 Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Proceed to section 7.2.

7.1.5 If the aliquot of the waste used for the preliminary evaluation (sections 7.1.1-7.1.4) was determined to be 100% solid at section 7.1.1.1, then it can be used for the section 7.2 extraction (assuming at least 100 grams remain), and the section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in section 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in section 7.3. The aliquot of the waste subjected to the procedure in section 7.1.1.7 might be appropriate for use for the section 7.2 extraction if an adequate amount of solid (as determined by section 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to section 7.2.10 of the nonvolatile TCLP extraction.

7.2 Procedure When Volatiles are not Involved. A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See section 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, see section 7.1.1), weigh out a subsample of the waste (100 gram minimum) and proceed to section 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in section 4.3.2 and is outlined in sections 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid-wash the filter if evaluating the mobility of metals (see section 4.4).

NOTE: Acid-washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains <0.5% dry solids (section 7.1.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing >0.5% dry solids (sections 7.1.1 or 7.1.2), use the percent solids information obtained in section 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see section 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in section 7.2.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (See section 7.2.12) or stored at 4°C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in section 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the waste contains <0.5% dry solids (see section 7.1.2), proceed to section 7.2.13. If the waste contains >0.5% dry solids (see section 7.1.1 or 7.1.2), and if particle size reduction of the solid was needed in section 7.1.3, proceed to section 7.2.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to section 7.2.11.

7.2.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in section 7.1.3. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20\times\text{percent solids (section 7.1.1)}\times\text{weight of waste filtered (section 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see section 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ±2 rpm for 18 ±2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ±2°C during the extraction period.

NOTE: As agitation continues, pressure may build within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ±2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in section 7.2.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see section 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the TCLP extract as follows:

7.2.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from section 7.2.12 is defined as the TCLP extract Proceed to section 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from section 7.2.12 with the initial liquid phase of the waste obtained in section 7.2.7. This combined liquid is defined as the TCLP extract. Proceed to section 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from section 7.2.7, is not or may not be compatible with the filtered liquid resulting from section 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the TCLP extract, and combine the results mathematically, as described in section 7.2.14.

7.2.14 Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH <2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4 °C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ± 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1)+(V_2)(C_2)}{V_1+V_2}$$

where:
V_1=The volume of the first phase (L).
C_1=The concentration of the analyte of concern in the first phase (mg/L).
V_2=The volume of the second phase (L).
C_2=The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles are Involved. Use the ZHE device to obtain TCLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4°C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (See section 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in section 4.6 are recommended for use under the conditions stated in sections 4.6.1—4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from section 7.3, section 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the waste is 100% solid (see section 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to section 7.3.5.

7.3.4 If the waste contains <5% dry solids (section 7.1.2), the liquid portion of waste, after filtration, is defined as the TCLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing >5% dry solids (sections 7.1.1 and/or 7.1.2), use the percent solids information obtained in section 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For wastes containing <5% solids (see Section 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing >5% solids (see Section 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (section 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle size reduction of the solid portion of the waste was required in section 7.1.3, proceed to section 7.3.6. If particle size reduction was not required in section 7.1.3, proceed to section 7.3.7.

7.3.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in section 7.1.3.1. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4°C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle size has been appropriately altered, proceed to section 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in section 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100% solid (see section 7.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to section 7.3.12.

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

If the original waste contained <0.5% dry solids (see section 7.1.2), this filtrate is defined as the TCLP extract and is analyzed directly. Proceed to section 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (See sections 7.3.13 through 7.3.15) or stored at 4°C under minimal headspace conditions until time of analysis.

Determine the weight of extraction fluid #1 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (section 7.1.1)} \times \text{weight of waste filtered (section 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See section 5.7).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary agitation apparatus (if it is not already there) and rotate at 30 ±2 rpm for 18 ±2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 22 ±3°C during agitation.

7.3.13 Following the 18 ±2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in section 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in section 7.3.9. All extract shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see sections 4.6 and 7.3.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

7.3.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from section 7.3.13 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from section 7.3.13 and the initial liquid phase (section 7.3.9) are collectively defined as the TCLP extract.

7.3.15 Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4°C until analyzed. Analyze the TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1)+(V_2)(C_2)}{V_1+V_2}$$

where:

V_1=The volume of the first phases (L).

C_1=The concentration of the analyte of concern in the first phase (mg/L).

V_2=The volume of the second phase (L).

C_2=The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to section 8.0 for quality assurance requirements.

8.0 Quality Assurance

8.1 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel.

8.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data are being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.2.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

8.2.2 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of TCLP extract as that which was analyzed for the unspiked sample.

8.2.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration of the TCLP extract when the recovery of the matrix spike is below the expected analytical method performance.

8.2.4 Matrix spike recoveries are calculated by the following formula:

$$\%R\ (\%\ \text{Recovery})=100\ (X_s-X_u)/K$$

where:

X_s=measured value for the spiked sample,

X_u=measured value for the unspiked sample, and

K= known value of the spike in the sample.

8.3 All quality control measures described in the appropriate analytical methods shall be followed.

8.4 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50% and the concentration does not exceed the regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

8.4.1 The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The fourth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and 150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrumental technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrumental signals or external-calibration-derived concentrations as the dependent variable (y-axis) versus concentrations of the additions of standard as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

84.4.4 Alternately, subtract the instrumental signal or external-calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject data to linear regression of the corrected instrumental signals or external-calibration-derived concentrations as the dependent variable versus the independent variable. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo TCLP extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES (DAYS)

	From: Field collection to: TCLP extraction	From: TCLP extraction to: Preparative extraction	From: preparative extraction to: determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Semivolatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA=Not applicable

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

[Appendix II—8.0 text revised at 57 FR 55117, Nov. 24, 1992]

TABLE 1—VOLATILE ANALYTES[1,2]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

[2] Benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichlorethane, 1,1-dichloroethylene, methyl ethyl ketone, tetrachloroethylene, trichloroethylene, and vinyl chloride are toxicity characteristic constituents.

TABLE 2—SUITABLE ROTARY AGITATION APPARATUS[1]

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA, (215) 343-4490	4-vessel (DC20S), 8-vessel (DC20), 12-vessel (DC20B).
Associated Design and Manufacturing Company	Alexandria VA, (703) 549-5999	2-vessel (3740-2), 4-vessel (3740-4), 6-vessel (3740-6), 8-vessel (3740-8), 12-vessel (3740-12), 24-vessel (3740-24).
Environmental Machine and Design, Inc	Lynchburg, VA, (804) 845-6424	8-vessel (08-00-00) 4-vessel (04-00-00).
IRA Machine Shop and Laboratory	Santurce, PR, (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitmore Lake, MI, (313) 449-4116	10-vessel (01VRE), 5-vessel (5VRE)
Millipore Corp	Bedford, MA, (800) 225-3384	4-ZHE or 4 1-liter, bottle extractor, (YT30ORAHW).

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 ± 2 rpm is acceptable.

TABLE 3—SUITABLE ZERO-HEADSPACE EXTRACTOR VESSELS[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA, (215) 343-4490	C102, Mechanical Pressure Device.
Associated Design and Manufacturing Company	Alexandria VA, (703) 549-5999	3745-ZHE, Gas Pressure Device.
Lars Lande Manufacturing[2]	Whitmore Lake, MI, (313) 449-4116	ZHE-11, Gas Pressure Device.
Millipore Corporation	Bedford, MA, (800) 225-3384	YT30090HW, Gas Pressure Device.
Environmental Machine and Design, Inc.	Lynchburg, VA, (804) 845-6424	VOLA-TOX1, Gas Pressure Device.

[1] Any device that meets the specifications listed in section 4.2.1. of the method is acceptable. a 110 mm filter.

TABLE 4—SUITABLE FILTER HOLDERS[1]

Company	Location	Model/ catalogue No.	Size
Nucleopore Corporation	Pleasanton, CA, (800) 882-7711	425910 410400	142mm, 47 mm.
Micro Filtration Systems	Dublin, CA, (800) 334-7132, (415) 828-6010	302400 311400	142 mm, 47 mm.
Millipore Corporation	Bedford, MA, (800) 225-3384	YT30142HW XX1004700	142 mm, 47 mm.

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

TABLE 5—SUITABLE FILTER HOLDERS[1]

Company	Location	Model	Pore Size (μm)
Millipore Corporation	Bedford, MA, (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA, (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ, (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA, (800) 334-7132, (415) 828-6010	GF75	0.7

[1] Any filter that meets the specifications in section 4.4 of the Method is suitable.

[Part 261, Appendix II]

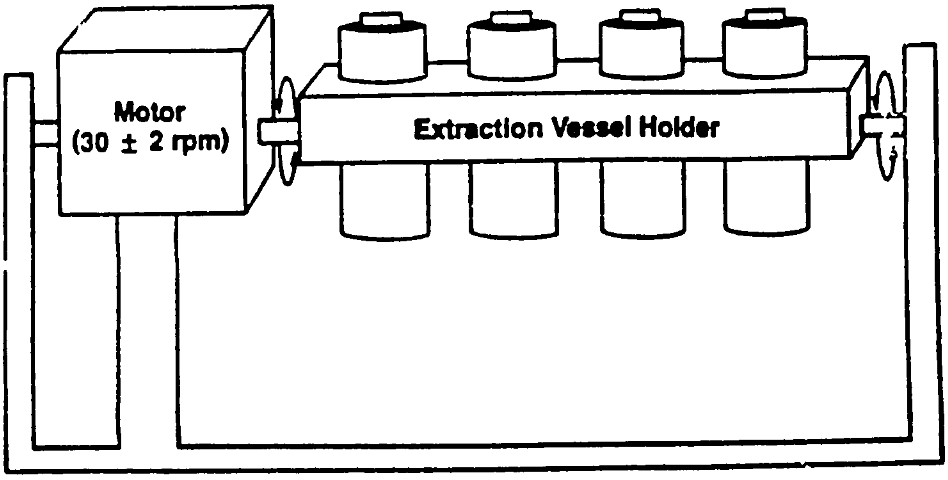


Figure 1. Rotary Agitation Apparatus

[Part 261, Appendix II]

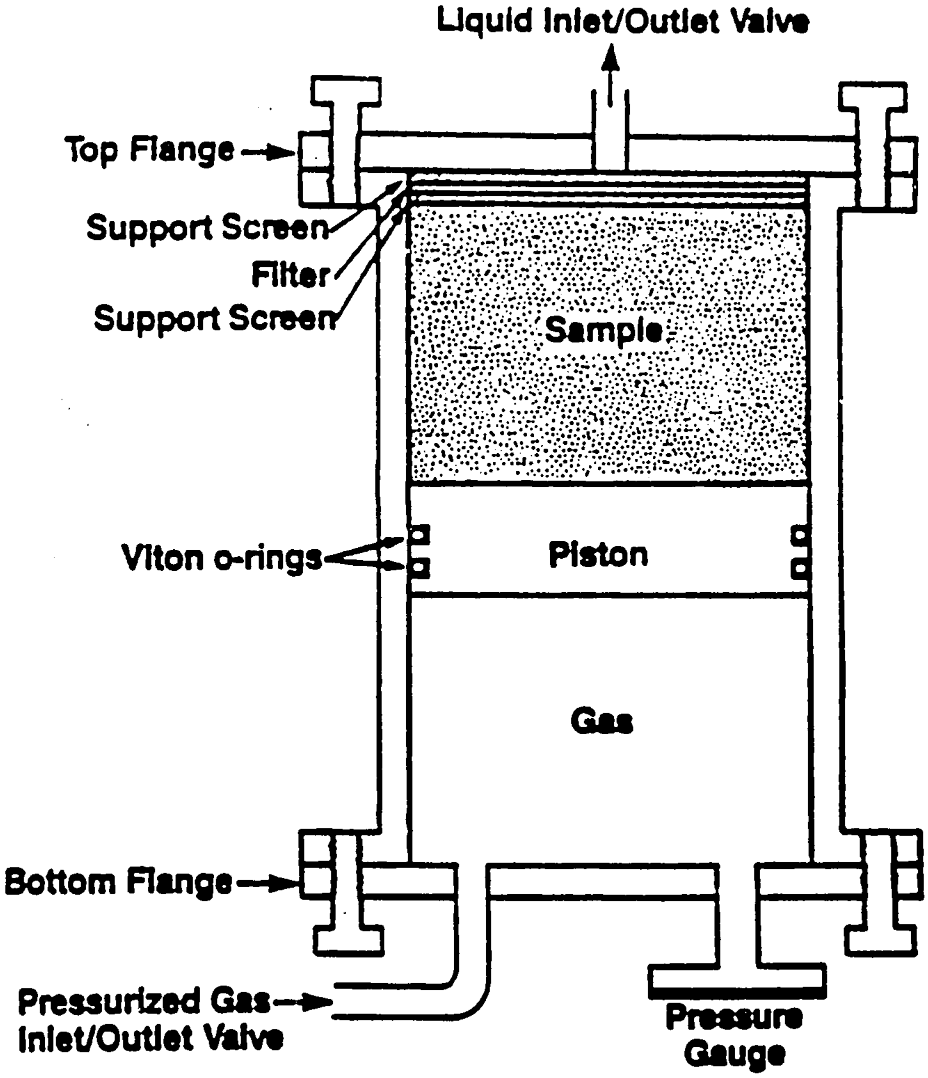
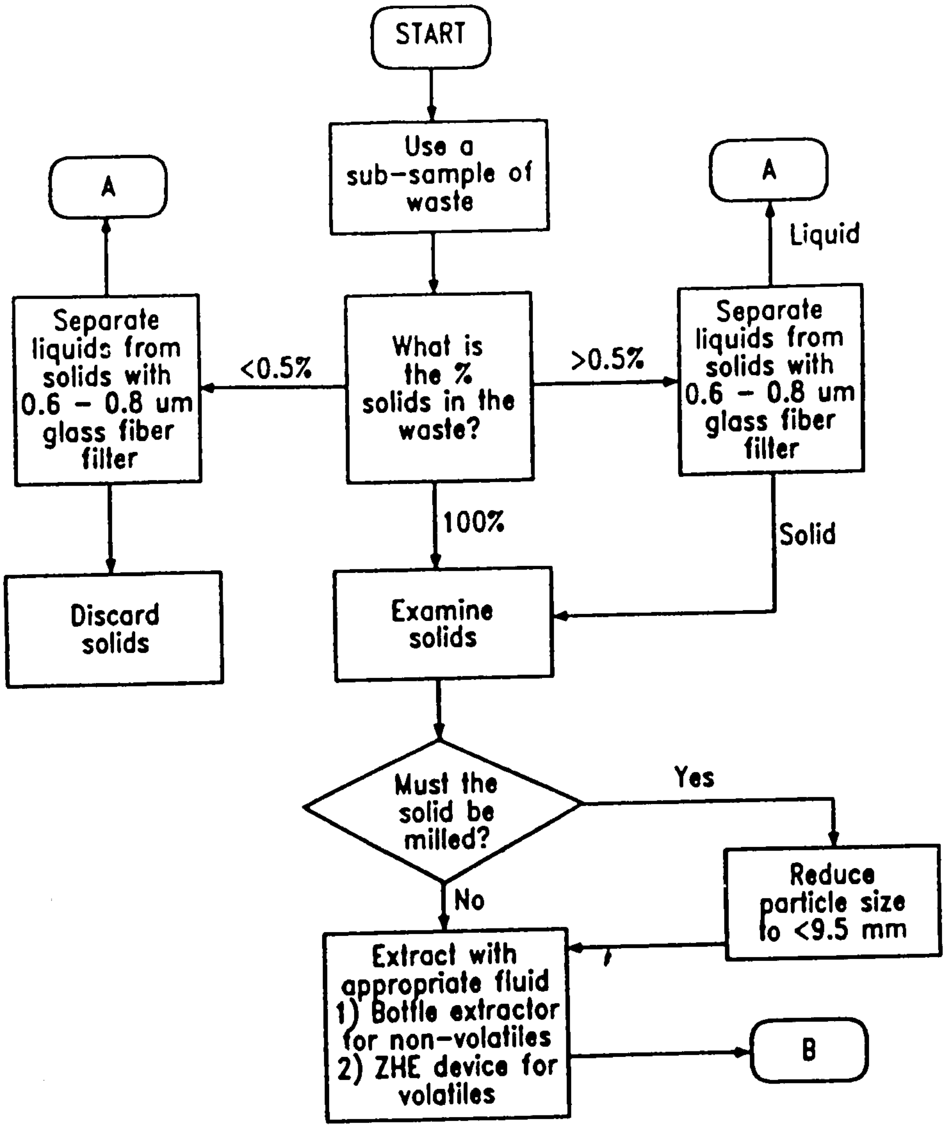


Figure 2. Zero-Headspace Extractor (ZHE)

[Part 261, Appendix II]

METHOD 1311

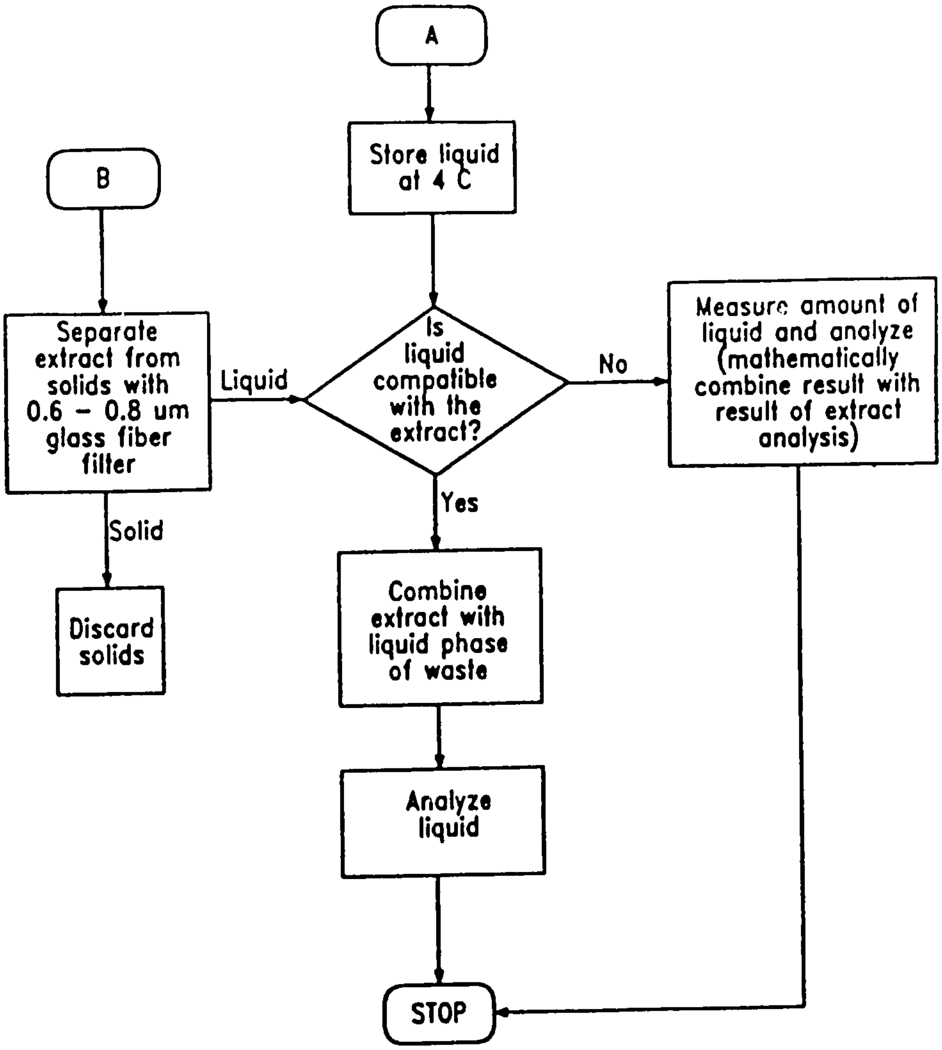
TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



[Part 261, Appendix II]

METHOD 1311 (CONTINUED)

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



[Part 261, Appendix II]

ATTACHMENT 5

UREA PLANT POLLUTION CONTROL

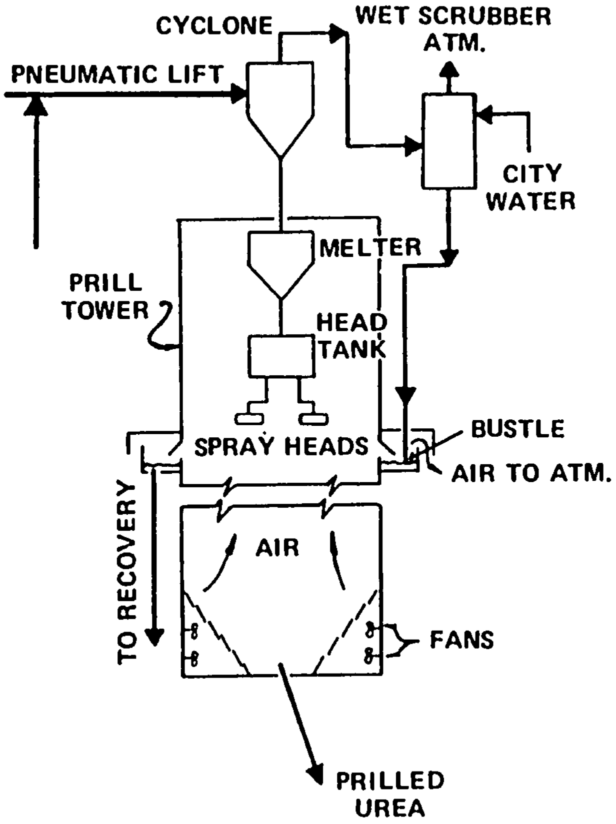
Good afternoon! My topic is "Urea Plant Pollution Control" and I will be discussing the control approaches used at the 700 ton per day Vistron urea plant located in Northwest Ohio. Vistron, incidentally, is a wholly-owned chemical subsidiary of Sohio -- more formally The Standard Oil Company of Ohio.

Our urea plant is part of the Vistron nitrogen complex consisting of units to produce 1500 T/D NH_3, 700 T/D urea, 650 T/D CO_2, 180 T/D nitric acid, 275 T/D ammonium nitrate, and the blending and shipping facilities necessary to handle this volume of production. This plant, which adjoins the Vistron acrylonitrile complex, is situated on the Ottawa River in Northwest Ohio about one mile downstream from the City of Lima, and immediately downstream from Sohio's 175,000 BPD refinery.

Many of you are aware that as the "exemplary" plant, the Vistron plant figured prominently in the development of EPA's urea plant effluent guidelines. This is a distinction we have viewed with mixed emotions -- and yours are probably more "mixed" than ours.

To understand why well over a million dollars have been spent in an effort to minimize urea unit losses, the receiving stream situation must be examined. The water supply for the City of Lima is from upground reservoirs charged largely with water pumped from the Ottawa River <u>upstream</u> from the City. Our plant discharges to the river <u>below</u> the City. Thus, for much of the year there is no natural flow at our point of discharge because the total natural flow has been impounded upstream for potable supply. This means Vistron must discharge its 2000 gpm effluent to a stream composed of about 12000 gpm of municipal sewage treatment plant effluent plus 3500 gpm of

Urea Prill Tower



treated refinery effluent. And that means that effluent quality must essentially that receiving water criteria suitable for a warm water fishery and other uses. Ammonia is a critical parameter. Obviously, this situation dictates extraordinary measures in Vistron's pollution control efforts. Recognizing this, engineering emphasis was directed during the urea unit design stages, toward minimizing losses to both air and water since surface run-off contaminated by fall-out from losses to the atmosphere would affect effluent quality.

Let us first look at the means devised to control losses to the air. Our unit, which is the C&I Girdler design, is a complete recycle process. Ammonia, CO_2, and recycled carbamate are fed to the reactor where they combine to form carbamate and urea. The liquid urea is separated from the carbamate in a series of flash separations. It is then routed to product tankage, or if prilled urea is desired, processing continues as the liquid is concentrated and prystallized. The crystals are then conveyed to the top of the prill tower by an air blower on top of the tower. The air-crystal mix passes through a cyclone separator, the crystals dropping into a melter, while the exiting air stream passes through a two-tray water scrubber where the urea dust is removed.

Of course, our major concern from a pollution standpoint is the air stream at rates up to 500,000 SCFM moving up the tower countercurrent to the falling urea droplets. This stream exits under the spray head deck through ten windows in the tower. At this level there is what we call a "bustle" around the outside of the tower (see slides I & II). Awnings on each of the ten windows direct the air downward across the water pond that encircles the tower in the bustle. The object of the system is to remove the urea dust, but unfortunately the system is capable of removing only the larger dust particles. Removal of the smaller particles is necessary to comply with air pollution control regulations, and that remains another problem.

While the unit design was not entirely successful in preventing air pollution, the scrubber on top of the prill tower is effective in absorbing the urea dust, and a certain amount is picked up in the bustle water. Obviously the more successful the air pollution control is, the greater the water pollution. Of course, the overall water pollution problem was recognized in the original design and its control had not been neglected. The general concept was that the urea-rich waste would be collected and fed to a specially designed stripper or hydrolyzer. In this tower the hydrolyzing, or decomposition of urea,would take place, leaving us with a relatively clean effluent, while the ammonia-rich overhead was recycled to the process. Well, just as we were disappointed with the process dust removal capability, so did we find the waste water system inadequate. In the first place, there was far more water than the hydrolyzer, which was designed for 60 gpm of feed, could handle. Furthermore, the tower's initial efficiency in destroying urea was much lower than we had expected.

So here we were with nearly a million dollars invested in waste control facilities and we couldn't meet state regulations for either air or water. In fairness to the designers, it should be noted that they had had no idea how restrictive those regulations would be. But for Sohio and Vistron, it was back to the drawing board. The water pollution was the most serious and that problem was attacked first. Working on both water problems simultaneously, hydrolyzer tower operating conditions were modified through on-stream testing until the tower's efficiency for urea removal was consistently high. The excess water problem was solved in two ways. It was decided that except for the 15 gpm of fresh water used in the scrubber atop the prill tower, and the wash-down water at that point, no new water would be brought into the system. But since calculations, based on early operating experience, indicated that there would still be more water than could be handled in the hydrolyzer, a concentrator was designed and installed. These two steps and the integration of the new system with the hydrolyzer have been very successful. The only water of any kind going to the river from the urea plant battery limits is the 60 gpm of lightly contaminated hydrolyzer bottoms. There is also a surface run-off stream which can become contaminated by prill tower fall-out.

The remainder of this paper will be directed to the details of how the water pollution control system works.

There is nothing especially unique in our reclaiming system and I offer my apologies to those who may have similar systems. However, because it is integrated with the hydrolyzing system, each must be understood.

The next slide shows the sections of the reclaiming system and the purpose of each.

SLIDE III RECLAIMING SYSTEM

1. Hot Solution Wash System

   To wash urea deposits from work areas and from equipment.

2. Urea Trenches

   To convey reclaimed urea to the urea drain tank.

3. Urea Drain Tank

   To serve as an accumulator of solution and a dissolver of urea solids.

4. Urea Rundown Tank

   To serve as storage for reclaimed urea solution and as a feed source for the concentrator and the hot wash system.

. Urea Concentrator

   To concentrate urea solution from about 20 wt. % urea to 75 wt. %.

All of this system, with the exception of the urea rundown tank, was added after the unit was in operation.

Now let's look at how each of these components serves its purpose. The next slide shows where the hot wash system is used.

<u>SLIDE IV</u>

HOT WASH SYSTEM

Main floor process building
Centrifuge floor
Screener floor
Melter and sprayhead floors
Prill collector floor
Prill tower ground floor

The wash system in the prill tower was integrated with the water systems already there for dust removal. Water from the vent scrubber on top of the prill tower, as well as any wash water from that area, gravitates to the bustle water pond. The pond provides wash water throughout the tower, with the excess overflowing to the lump dissolving drum or the prill tower trench. If the urea is contaminated, it is always collected in the prill tower trench and flows to the steam jacketed urea drain tank. This tank is below ground level to permit the sewer system to gravitate to it. This sewer network surrounds all areas in the urea unit where either liquid or dry urea might be spilled.

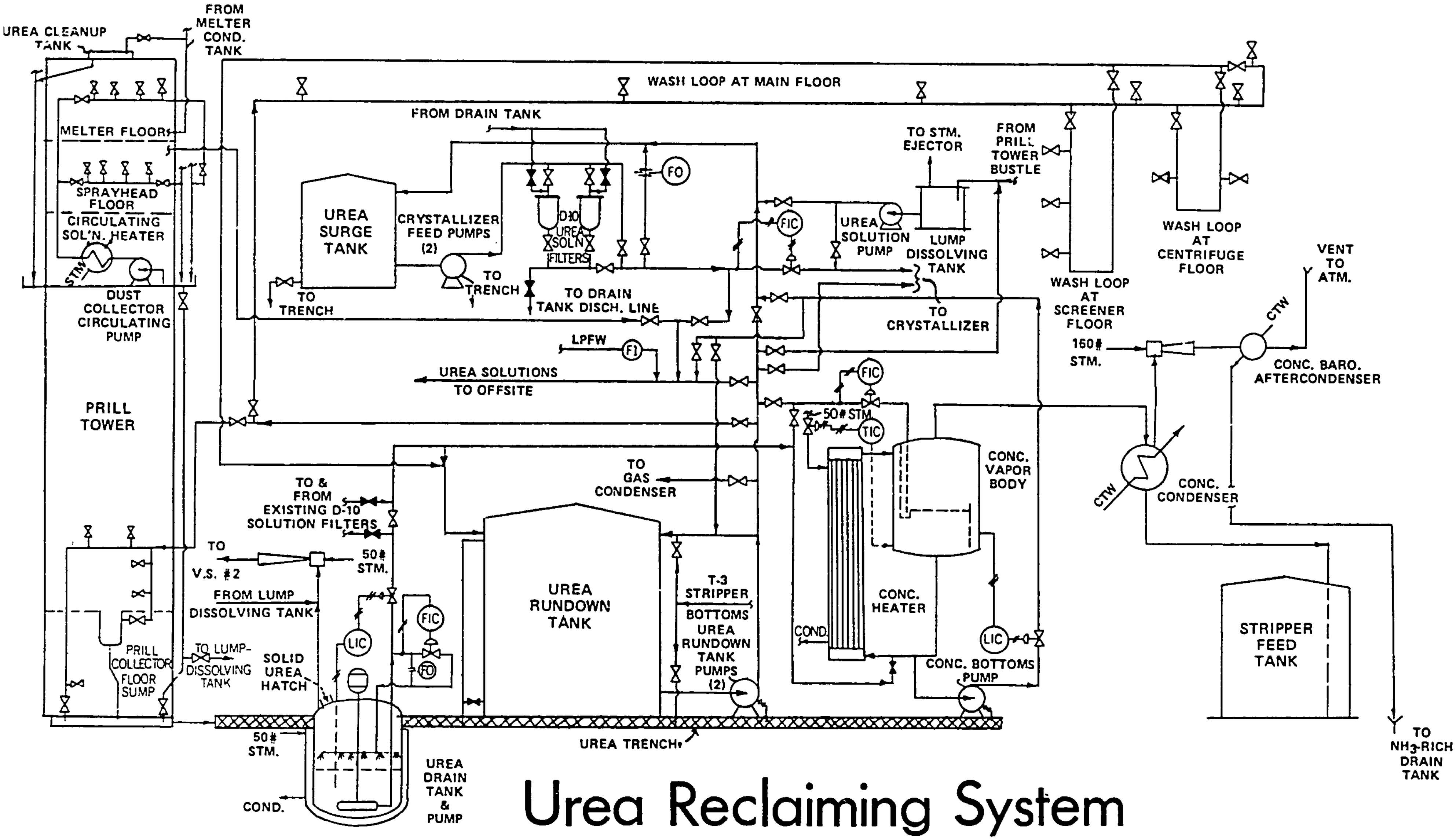
In addition to receiving the wash water, the urea drain tank is the recipient of all the scrap solid urea from the warehouse and other areas. The solids are dumped into a hopper in which there is a sparger fed with hot solution wash water. The dissolved scrap with some floating lumps flows into the sewer and thence to the urea drain tank.

The lumps are caught by a screen at about mid-level in the tank. The sump pump maintains continuous circulation through a spray header above the screen, thus dissolving the solids. It also transfers solution on level control through a leaf filter to the urea rundown tank. Because the filter has to be cleaned by Maintenance twice a week, it has to be spared.

From the rundown tank the urea solution, which is normally at about a 20% strength, is reused as a hot wash or it is pumped to the concentrator. The concentrator system consists of a flash vessel with one bubble cap wash tray, a reboiler, an overhead condenser and twin ejectors which hold the pressure at 4 psia. The feed enters above the wash tray scrubbing any entrained urea from the rising vapors. It then overflows into a downcomer to the bottom of the vessel before passing to the reboiler which is on temperature control set to produce a 75% liquid urea product.

The system is operated under a vacuum to minimize the loss of urea through decomposition. As this cannot be entirely eliminated, the NH_3-rich overhead condensate is routed to the hydrolyzer feed tank as is the condensate from each ejector. The feed rate to the concentrator varies, of course, depending upon the amount of clean-up underway but normally runs about 30 gpm. Occasionally, it is possible to shut the system down altogether.

The next slide provides a sketch of the whole system. This reclaiming system works well and with a minimum of operating problems. It recovers a lot of urea for us and it keeps major pollution out of the river. But in itself, it comes nowhere near enabling us to meet EPA standards. For the final clean-up, we must turn to the hydrolyzer which I have mentioned briefly before. This tower handles both the urea-and ammonia-contaminated streams shown on the next slide.



Urea Reclaiming System

SLIDE VI HYDROLYZER FEEDS

The NH_3 rich sewer system

Condensate from crystallizer ejector hot well

Condensate from flash drum pre-condenser

Condensate from the concentrator condensers

The tower is designed for a 60 gpm feed rate. The overhead, which is rich in ammonia and carbon dioxide, is returned to the process. Removal efficiency for both urea and ammonia is high, leaving a bottoms stream with an average of 87 ppm ammonia and 130 ppm urea. The next slide compares the results with EPA guidelines for prilled urea plants started after January 1, 1970.

SLIDE VII VISTRON VS EPA GUIDELINES

Source	Pounds per 1000 Pounds Product (Average)		EPA Guidelines	
	NH_3-N	Urea-N	NH_3-N	Urea-N
Hydrolyzer Bottoms	0.047	0.057		
SRO* New Plant		0.072		
B & S** + SRO (Old Plant)		0.219		
TOTAL	0.047	0.348	0.05	0.67

* SRO - Surface Run-off, including dust fall-out

** B & S - Blending and Shipping

Before closing, I should say that as yet we have not been as successful in solving the air pollution problem. We do, however, have a system designed that will bring the particulate emissions within limits.

Thank you for your kind attention.

Jay M. Killen

Presentation at The Fertilizer Institute
Environmental Symposium
January 14-16, 1976
Fairmont Hotel
New Orleans, Louisiana

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CURRICULUM VITAE

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1953 - B.Ch.E. Rensselaer Polytechnic Institute, Troy, N.Y.

1953-55 - Chemical Engineer Trainee, American Cyanamid Co., N.Y. N.Y.

1956 - Project Engineer - Engineering and Construction Division, American Cyanamid Co., N.Y. N.Y.

New Venture Studies; project engineer on design and construction of synthetic fibers plant.

1959-67 - Plant Engineer - Brewster Phosphate Chemical and Mines, American Cyanamid Co., Brewster, FL

Supervised plant engineering department for assistance to operations in maintenance, alterations and improvement projects.

1967-75 - Chief Process Engineer - White Springs, FL Phosphate Chemical Processing Plant, Occidental Chemical Co., White Springs, FL

Supervised process engineering, environmental control and analytical laboratory departments.

1975-79 - Chief Process Engineer - Design and Construction Project for new Chemical Complex, Occidental Chemical Co., White Springs, FL

1979-86 - Manager, Environmental Control, White Springs facility now including two Chemical Complexes and 2 mines to produce fertilizer intermediates, Occidental Chemical Co., White Springs, FL

Duties included supervision of State and Federal regulatory affairs environmental permitting and control activities covering air, water and dredge-fill.

Supervised first CORPS 404 Wetland Mining EIS in United States leading to a CORPS 404 permit to continue mining at location.

1987-92 - Environmental Special Projects Manager, Occidental Chemical Co., White Springs, FL

Primarily responsible for creating, designing, permitting of special waste abatement projects leading to both reduction in environmental impacts and permitting of new outfalls to insure continuation of major phosphate mining and fertilizer chemical processing complex.

1993-94 - Consulting Engineer

Clients:

- The Fertilizer Institute
  501 Second Street NE
  Washington, DC

  RE: Environmental Regulation Studies

- World Environment Center
  419 Park Avenue South, Suite 1800
  New York, NY

  RE: Environmental Review at Kedainiai State Chemical Plant, Lithuania

Other Associations

1965-66 - Vice-Chairman and Chairman - Central Florida A.I.Ch.E.

1978-80 - Vice-Chairman and Chairman, Manufacturing Environmental Committee of The Fertilizer Institute

(A 40 member standing committee. Have been on it since 1974. Representatives appointed by officers of about 35 major US fertilizer companies)

1968-88 - Florida Section, National Air and Waste Management Association

1975 - Annual Program Chairman
1980-83 - Director
1984-85 - Secretary-Treasurer
1985-86 - Vice-Chairman
1986-87 - Chairman