

Topics of This Seminar

- Background of the certified qualification
- Required knowledge to become a certified environmental analyst
- Measurement law system in Japan
- Problems of the current Japanese measurement law system
- How to cope with the problems
- What are necessary to keep accuracy management in analysis of industrial wastewater quality
- Recommendations
- Others



Pre-treatment apparatus
(TOYOTA Chemical Engineering)

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Background of Certified Environmental Analyst System

- To secure reliability and accuracy in environmental analysis
- An indispensable registration criteria as personnel asset (full-time employee) to open measurement certification business of concentration of substances in soot, water, soil or noise level,
- At least one certified environmental analyst in a laboratory
- Measurement certification report is legally required the signature of the certificated environmental analyst.



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Required Knowledge and Responsibilities of Certified Environmental Analyst

- High degree of measurement knowledge and techniques
- Comprehensive measurement management from plan and design of measurement to implementation of measurement and evaluation of analysis results, such as;
 - How to take a sample,
 - Selection and decision of analysis or measurement,
 - Evaluation of the analysis results,
 - Maintenance and inspection of analyzers,
 - Preparation of analysis report,
 - Improvement of measurement methods,
 - Education of the measurers,
 - Others necessary to secure accurate measurement and analysis



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How to become the Certified Environmental Analyst

- To pass Certified Measurer National Examination (once a year) + Practical experience, etc.
 - Registration, Passing rate of the examination is around 10 %.
- Training course given by National Institute of Advanced Industrial Science and Technology + Practical experience + Certification by Measurement Administration Council (twice annually) →Registration



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Required Knowledge for the Examination

No.	Certified Environmental Analyst concerning concentration	Certified Environmental Analyst concerning noise and vibration
1	Basic knowledge of environmental measurement	
	Basic knowledge of environment relating laws and chemistry	Basic knowledge of environment relating laws and physics
1) A	<p>1) Environment relating laws: The Basic Environment Law, Air Pollution Control Law, Water Pollution Control Law, Offensive Odor Control Law</p> <p>2) Chemistry</p> <ul style="list-style-type: none"> • Basic knowledge of physical chemistry: Law of Avogadro, Chemical Thermo-dynamics, etc. • Phase equilibrium: Thermo-dynamics of mixed gases, nature of solutions, law of distribution, etc. • Chemical equilibrium and reaction velocity • Structures and natures of substances: Kinds of atomic bonds, kinds of oxidation and reduction agents, chelating agents, surfactants, etc. • Structures and natures of organic compounds: Substitution reaction, addition reaction, elimination reaction, etc. • Qualitative analysis of organic compounds: Chemical actions of reaction agents • Others: Atomic nucleus disintegration, etc. 	<p>1) Environment relating laws: The Basic Environment Law, Noise Regulation Law, Vibration Regulation Law</p> <p>2) Physics</p> <ul style="list-style-type: none"> • Unit • Classical dynamics: Kinetics equation, gravity kinetics, simple oscillation, Circular movement with uniform velocity, Elasticity and wave motion, etc. • Physical optics: Refraction of substances, optic interference, refraction and dispersion, etc. • Electromagnetism: Static electricity, stable electric current, electromagnetic field, electromagnetic induction, etc. • Others: Thermo-dynamics, etc.
2) B	Outline of chemical analysis and measurement of concentration	Outline of noise and vibration and measurement of sound pressure level and oscillating acceleration level
1) B	<p>1) General application of chemical analysis</p> <p>2) Knowledge of basic principals of analyzers, handling, maintenance and others concerning general knowledge of measurement and analysis</p> <ul style="list-style-type: none"> • Foundation of chemical analysis: Classification of analysis methods, performances of analyzer • Meanings of measured results • Reliability of analysis results • Management of measurement instruments: Calibration of measurement instruments, maintenance items • Preparation of calibration curve: Absolute calibration, internal standard, standard addition method and remarks 	<p>1) Knowledge of natures of sound and vibration</p> <p>2) General knowledge of measurement of sound pressure level and oscillating acceleration level</p> <ul style="list-style-type: none"> • Basic knowledge of noise and vibration: Basic knowledge of sound, vibration and wave motion, unit of sound, Indication of vibration level, sound wave generation and nature of sound source, transmission of sound wave, transmission of wave motion, calculation of dB, etc. • Influence of noise • Noise meter: Calibration of noise meter, noise recorder, frequency analysis • Noise measurement: Measurement of noise level, measurement of power level, measurement of sound reduction materials, frequency analysis

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Required Knowledge for the Examination

No.	Certified Environmental Analyst concerning concentration	Certified Environmental Analyst concerning noise and vibration
2	Outline of chemical analysis and measurement of concentration	
	Outline of chemical analysis and measurement of concentration	Outline of noise and vibration and measurement of sound pressure level and oscillating acceleration level
1) B	<p>2) Knowledge of basic principals of analyzers, handling, maintenance and others concerning general knowledge of measurement and analysis</p> <ul style="list-style-type: none"> • Chromatography: Gas-Chromatography, High Performance Liquid Chromatography, Ion-Chromatography, etc. • Spectroscopy: X-ray Fluorescence Analysis, absorptometry, Fluorescence Spectrophotometer, Infrared spectrophotometry, Atomic absorption method, Chemoluminescence, Nuclear Magnetic Resonance, Mass analysis, Activation Analysis, Inductively Coupled Plasma (ICP) atomic emission spectrometry, etc. • Electric-Chemical method: Conductimetry, coulometry, ion-selective electrode method, etc. • Analysis of inorganic compounds: Pre-treatment, cation-ion separation, titration, weight analysis, etc. • Soot analysis: Sampling, pre-treatment, SO_x, NO_x, O₃, omdant, CO, HC, dust, SP, Cl, HCl, F, NH₃, H₂S, etc. • Water analysis: Sampling, pre-treatment of sample, SS, pH, DO, BOD₅, COD, TOC, TOD, n-hexane extract, phenol, TDS, Anion-surfactant, F, CN, NH₄-N, NO₂-N, NO₃-N, Org-N, T-N, P, coliforms, Cu, Cd, Pb, Cr, Hg, As, V, Mn, etc. • Soil, industrial waste, food analysis 	<p>2) General knowledge of measurement of sound pressure level and oscillating acceleration level</p> <ul style="list-style-type: none"> • Noise control: How to control noise, countermeasures of noise source, prevention of sound transmission, noise transmission in building and prevention, sound absorption materials, sound-cut materials • Vibration pollution: Influence of vibration, evaluation of ISO vibration exposure • Vibration meter: Principal and structure, etc., maintenance management, standard of vibration level meter, calibration of vibration meter, vibration measurement • Measurement of oscillating acceleration level: Plan of measurement of vibration • Measurement of oscillating acceleration level • Prevention of vibration: Vibration generation and prevention of vibration, elasticity support, elasticity support materials, vibration prevention countermeasures

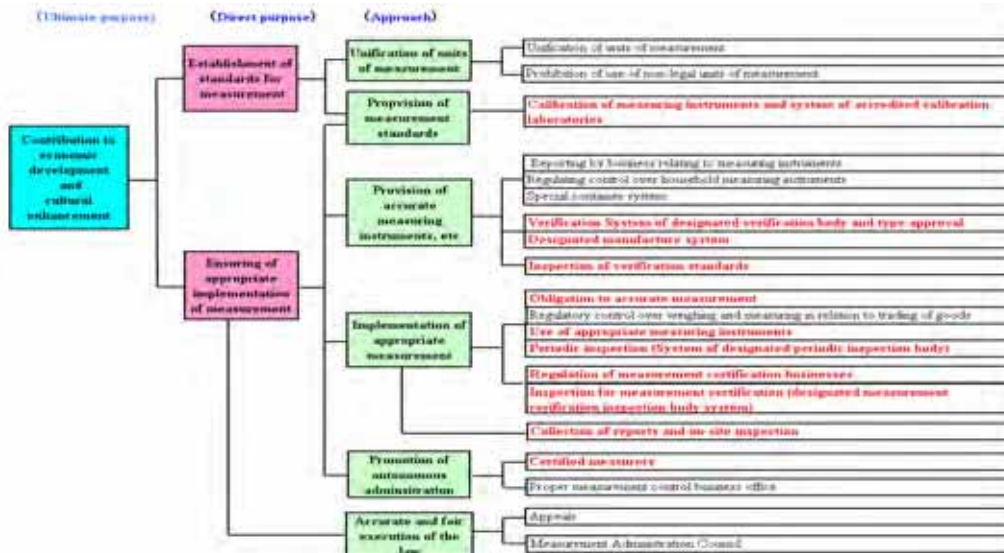
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Required Knowledge for the Examination

No.	Certified Environmental Analyst concerning concentration	Certified Environmental Analyst concerning noise and vibration
3	Laws concerning measurement	
	1) Objective and definition of measurement law 2) Measurement unit, etc. 3) Regulation of measurement instruments, etc. 4) Implementation of accurate measurement 5) Measurement certification business 6) Appropriate measurement management: Measurers, appropriate measurement management office system, etc. 7) Calibration of measurement instruments, etc: Traceability system, 8) Other regulations and punishment	
4	Outline of measurement management	
	1) Measurement plan: Objectives of measurement, methods and selection of measurement instruments, data transmission, calibration and S/N ratio, Accuracy management of measurement instruments, standardization of measurement works 2) Measurement system design: Outline of automatic measurement 3) Quality control: Errors and accuracy in measurement 4) Sampling and random sampling inspection method 5) Data management: Statistical treatment of the measured figures 6) Other general knowledge concerning measurement: definitions of measurement methods, Dynamic characteristics of measurement instruments: Deflection and zero method, maintenance and reliability of measurement instruments; control chart method and design of experiment	

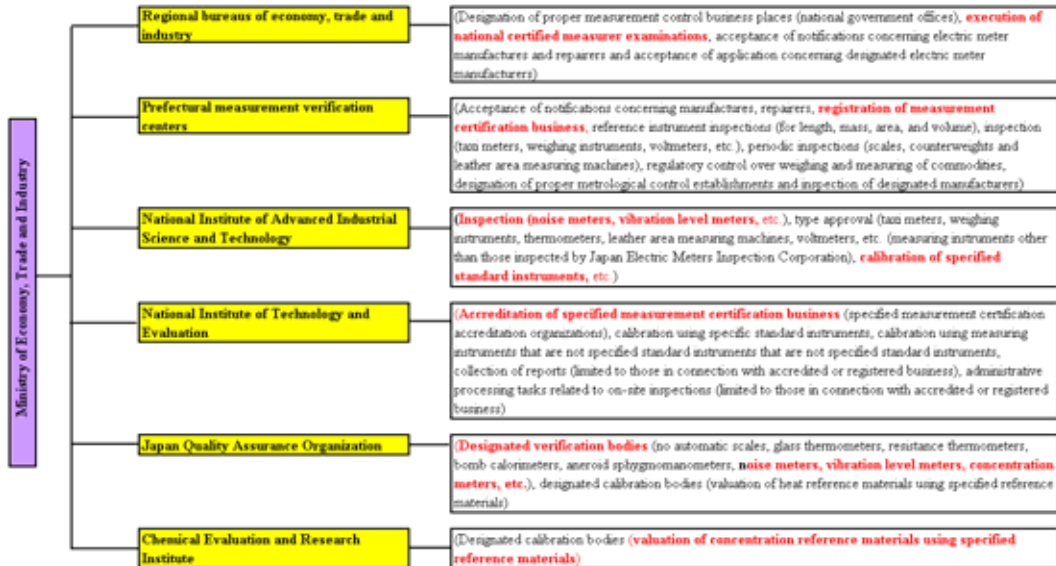
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Structure of the Measurement Law (JETRO, Feb.2007)



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Related Institutions to the Measurement Law



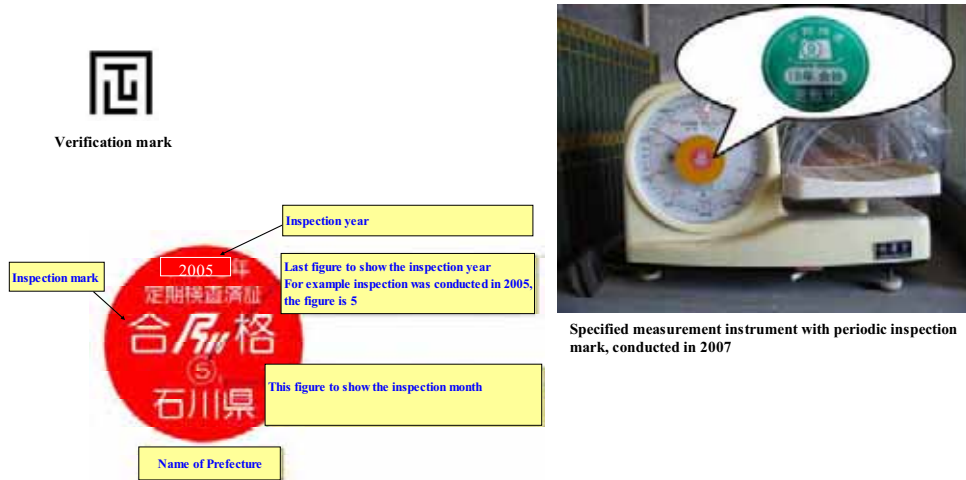
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Key Points of the Measurement Law

- Measuring instruments are needed fit for official guarantee of accuracy
- Specified measuring instruments must meet set accuracy standards through methods such as verification and/or periodic inspection to check their conformity to set technical standards in terms of structure and instrumental error.
- Don't use specified measuring instruments without verification mark or periodic inspection mark.

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Verification and Periodic Inspection Mark



Specified measurement instrument with periodic inspection mark, conducted in 2007

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Acceptable error of vessel for measuring volume

Name	Acceptable error
100 ml Mess cylinder	1/200 ±0.5 ml
100 ml Mess flask	0.10% ±0.1 ml
25 ml hole pipette	0.10% ±0.03 ml
25 ml burette	0.10% ±0.03 ml

At 20 °C



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Specified measuring instruments used for certification of noise/ vibration level or concentration

Name of Specified Measurement Instrument
• Ordinary noise meter and precise noise meter
• Vibration level meter
• Glass electrode pH meter
Automatic Air Monitoring Analyzer
• Oxygen meter using zirconium (maximum level: 5 to 25 v/v %)
• Magnetic oxygen meter (maximum level: 5 to 25 v/v %)
• SO ₂ meter using electricity conductivity (maximum level: more than 50 v/v ppm)
• SO ₂ meter using ultra violet (maximum level: more than 50 v/v ppm)
• NO _x meter using ultra violet (maximum level: more than 25 v/v ppm)
• Non- dispersion infrared rays SO ₂ meter
• Non- dispersion infrared rays NO _x meter
• Non- dispersion infrared rays CO meter (minimum scale: less than 100 v/v ppm and 100 to 200 v/v ppm with maximum level of 5 v/v %)
• Chemical luminescence NO _x meter (maximum level: more than 25 v/v ppm)



Noise Meter (RION)

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Parties not necessary registration as a measurement certification business

- ◆ National and local public organizations
- ◆ Some independent administrative institutions
 - National Institute of Advanced Industrial Science and Technology,
 - National Institute of Technology and Evaluation,
 - National Institute of Occupational Safety and Health,
 - Japan and National Institute for Environmental Studies
 - Organizations registered under another law

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Classification of environmental measurement certification business

- Relating to the concentration of substances in air, water or soil, excluding specified substance (dioxins)
- Relating to the concentration of dioxins in air, water or soil (Accredited certified measurement business for specified concentration (only dioxins))
- Sound pressure level
- Oscillating acceleration level

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Registration Criteria

- Arrangement of measurement instruments
- Arrangement of certified environmental measurer (analysts)
- Copy of accreditation (only for specified measurement certification)



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Required documents for registration

- Outline of the company, certificates of the company's regime
- Outline of measurement certification business
 - planned number of measurement certification, objects of the measurement such as concentration, vibration, noise
- List of instruments, facilities and equipment for measurement
 - Name, type, specification, installation place
- Measurement methods along with instruments, facilities and equipment for measurement (Note)
(Environmental measurement certification relating to the concentration)
- Copy of the certified environmental analyst
- Copy of the health insurance card of the certified environmental measurer (analyst)
- Copy of acceptance of wastewater and air pollution control facilities
(Environmental measurement certification relating to the concentration of a substance in air, water or soil, excluding specified substances (dioxins) and measurement certification relating to the concentration of dioxins in air, water or soil)
- Copy of accreditation by National Institute of Technology and Evaluation or Japan Chemical Laboratory Association.
(Specified measurement certification business)
- Floor plan to show the installations and storage of instruments, facilities, equipment for measurement certification, and laboratory
- Information map to the laboratory from the nearest station

Note:

- 1) As for the specified measuring instruments (except pH meter), copies of verification certifications by IQA (Japan Quality Assurance Organization) for specified measuring instruments or inspection certifications to meet criteria by designated manufacturers to be attached.
- 2) As for the level recorder used with noise meter or oscillating acceleration level meter, copy of inspection certification by IQA (Japan Quality Assurance Organization) to be attached

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List of analyzer, facilities and equipment for measurement of concentration and specified concentration of water or soil

A. Facilities necessary for registration application designated by Ministry of Economy, Trade and Industry		
No.	Specified measurement instruments and other equipment and facilities	Required performance
1	Analysis instruments, apparatus and standard substances	Refer to B and C for analysis instruments
2	Mass balance (Electronics scale, etc.)	Weighing more than 100 g with the scale of less than 1mg
3	Pure water production apparatus or pure water	Ion-exchange or distillation type
4	Exhausted gas treatment facility	To prevent target substances from discharging
5	Wastewater treatment facility	To prevent target substances from discharging
6	Glass electrode pH detector	-
7	Glass electrode pH indicator	-

B. An example of analysis instruments or apparatus necessary for analysis methods of the target parameters			
No.	Analysis instruments or apparatus	No.	Analysis instruments or apparatus
1	Glass-made thermometer	11	Inductively Coupled Plasma (ICP) atomic emission spectrometry
2	Electric thermometer (thermocouple/resistance type)	12	ICP-Mass spectrometry
3	Atomic Absorption Spectrophotometer	13	Ion- chromatograph
4	Mercury analysis apparatus	14	Ion selective electrode
5	Gas Chromatograph	15	Spectrophotometer
6	Gas Chromatograph-Mass Spectrometry	16	Fluorescence Spectrophotometer
7	High Performance Liquid Chromatograph	17	Purge-trap concentration apparatus
8	DO meter	18	Headspace concentration apparatus
9	Automatic pH meter	19	Automatic DO analyzer
10	Automatic COD analyzer		

C. An example of equipment necessary for analysis			
No.	Equipment	No.	Equipment
1	Drier to get a fixed weight	6	Microwave ashing system
2	Water bath	7	Shaker
3	Centrifuge	8	Incubator
4	Electric furnace	9	Automatic titration apparatus
5	Concentration apparatus: Distillation, Extraction, Separation Column, etc	10	Fume hood

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Issuance of Registration

◆ On-site inspection to confirm the application by prefectural measurement verification centers

- Existence and location of the enterprise and laboratory
- Rolls and authorities of certified environmental analyst
- Measurement instruments, equipment and facilities reported
- Necessary date of issuing registration: about 15 days after receiving application



Fume Hood

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Items to be regulated in the business regulations

To submit the business regulations to the prefectural governor **within three months** after the registration.

- ◆ Classification of measurement certification business
- ◆ Organization chart and rolls
- ◆ Methods of measurement (JIS, regulations, notices, etc by Ministries with the enacted year)
- ◆ Keeping, maintenance, inspection and correction of the specified measurement instruments and other measurement instruments, equipment and facilities
- ◆ **Matters concerning measurement certification report including:**
 - Declaration of measurement certification
 - Number of measurement certification and date of issuing measurement certification
 - Name, address, registration number of the enterprise issuing measurement certification
 - Name of the certified environmental analyst and registration number
 - Customer's name
 - Name of the sample
 - Date of taking sample and by who
 - Parameters to be measured
 - **Measurement method of each parameter**
 - Measurement result
 - **Minimum limit of determination**
 - In case of partially out-sourcing, name, address of the out-sourcing measurement certification business and concrete description of parameters
 - Others like origin of the sample
- ◆ Execution report of measurement certification and storage of certification report
- ◆ Matters concerning partially out-sourcing
- ◆ Others necessary for measurement certification business

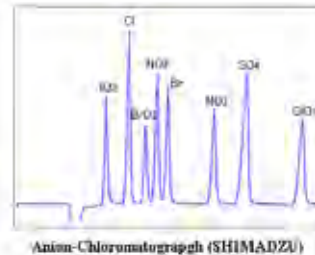


Purge & trap concentration monitor (CDS Analytical Inc.)

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On-site inspection by prefectural measurement verification center

- ◆ Approximately every three years
- ◆ Inspection includes management and technical aspects
 - (Management aspects)
 - If the certified environmental analyst is doing his/her obligations properly
 - If the business regulations are in conformity to actual situation
 - If each process from receiving order to analysis or measurement and issuance of certification report is working properly
 - Others
 - (Technical aspects)
 - If the measurement instruments are well maintained
 - If the measurement methods and procedures are appropriate
 - If technical improvement is continuously implemented
 - If the preparation of certification report and the contents are appropriate
 - If the accuracy management is appropriate



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An Example of Minimum Limit of Determination and Significant Figure-1

	Parameter	Unit	Minimum limit of Determination of River Water	Environmental criteria (River water)	Significant figure
Parameters for life environment	pH		-	6.5 -8.5*	2
	Dissolved Oxygen (DO)	mg/l	0.5	7.5*	3
	Biochemical oxygen demand (BOD ₅)	mg/l	0.5	1*	2
	Chemical oxygen demand (CODMn)	mg/l	0.5	-	2
	Suspended solid (SS)	mg/l	1	25*	2
	Total coliform	cfu/100 ml	1	50*	2
	n-hexane extract	mg/l	1	-	2
	Total Nitrogen as N	mg/l	0.03	-	2
	Total phosphorus as P	mg/l	0.003	-	2
	Cadmium (Cd)	mg/l	0.001	0.01	2
Parameters concerning human health	Total cyanide (CN)	mg/l	0.001	ND	2
	Lead (Pb)	mg/l	0.001	0.01	2
	Hexavalent chromium (Cr ⁶⁺)	mg/l	0.005	0.05	2
	Arsenic (As)	mg/l	0.001	0.01	2
	Total mercury (T-Hg)	mg/l	0.0005	0.0005	2
	Alkyl-Hg	mg/l	0.0005	ND	2
	Poly Biphenyl Chloride (PCB)	mg/l	0.0005	ND	2
	Di-chloromethane	mg/l	0.002	0.02	2
	Butyl chloride carbon (CCl ₄)	mg/l	0.0002	0.002	2
	1,2-dichloroethane	mg/l	0.0004	0.004	2
	1,1-dichloroethylene	mg/l	0.002	0.02	2
	cis-1,2-dichloroethylene	mg/l	0.004	0.04	2
	1,1,1-trichloroethane	mg/l	0.1	1	2
1,1,2-trichloroethane	mg/l	0.0006	0.006	2	
Tri-chloroethylene	mg/l	0.003	0.03	2	

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An Example of Minimum Limit of Determination and Significant Figure-2

	Parameter	Unit	Minimum limit of Determination of River Water	Environmental criteria (River water)	Significant figure
Parameters concerning human health	1,3-dichloropropene	mg/l	0.002	0.0002	2
	Thiuram	mg/l	0.0006	0.006	2
	Simazine	mg/l	0.0003	0.003	2
	Thiobencarb	mg/l	0.002	0.02	2
	Benzene	mg/l	0.001	0.01	2
	Selenium (Se)	mg/l	0.001	0.01	2
	NO ₂ -N and NO ₃ -N as N	mg/l	0.06	10	3
	Fluorine (F)	mg/l	0.1	0.8	2
	Boric acid (B)	mg/l	0.1	1	2
	Special parameter**	Phenols	mg/l	0.005	0.005**
Copper (Cu)		mg/l	0.01	1**	2
Zinc (Zn)		mg/l	0.05	1**	2
Iron (Fe)		mg/l	0.05	0.3**	2
Manganese (Mn)		mg/l	0.01	0.05**	2


Note

* Standard for Classification AA (most clear water)

** Standard for drinking water

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No. 1608



Measurement Certificate

21st April 2006

Client Name: _____

Registration number of Environmental Certification business: _____
Company's name, TEL with Seal: _____
Name of Certified Analyst with his seal: _____

I certify the measurement results of the sample dated 11 April 2006 as the followings.

Record

Name of Sample, Location of sampling, Date and hour of sampling, Name of Sampler and company's name, Weather, Atmosphere and water temperature		
Parameter	Measurement Result	Method of Measurement
Cadmium and its compounds (Cd)	Less than 0.01 (mg/l)	JIS K 0102 55.1
Lead and its compounds (Pb)	0.02 (mg/l)	JIS K 0102 54.1
Hexavalent chromium (Cr ⁶⁺)	Less than 0.05 (mg/l)	JIS K 0102 65.2.1
Arsenic and its compounds (As)	Less than 0.01 (mg/l)	JIS K 0102 61.2
Mercury and its compounds (Hg)	Less than 0.005 (mg/l)	Appendix chart 1, Notice by Ministry of Environment, 1971
Total iron (Fe)	0.22 (mg/l)	JIS K 0102 57.2
Copper and its compounds (Cu)	0.07 (mg/l)	JIS K 0102 52.2
Selenium and its compounds (Se)	Less than 0.01 (mg/l)	JIS K 0102 67.2
End		
Remarks: "less than" means less than minimum limit of determination		
Person's name in charge of measurement		

An Example of Measurement Certificate

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Problems of Current Measurement Law

1 Background

- 1) Globalization of economic activities
- 2) Necessity of trace concentration measurement
- 3) Rapid increase of substances regulated to be measured

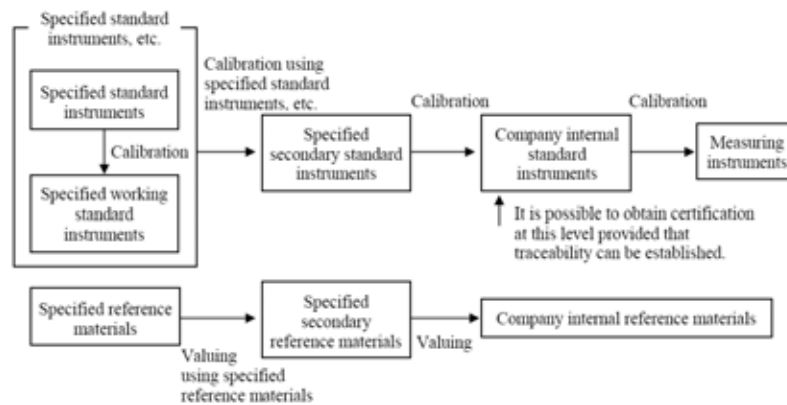
2 Current problems of the measurement Law

- 1) Japanese environmental measurement certification system is not well known in the world.
 - Number of certified environmental analysts is more than 10,000 and the registered certified environmental measurement enterprises are more than 1,500.
- 2) Insufficient management ability
- 3) The ability of the certified environmental analyst can't catch up with the current trend

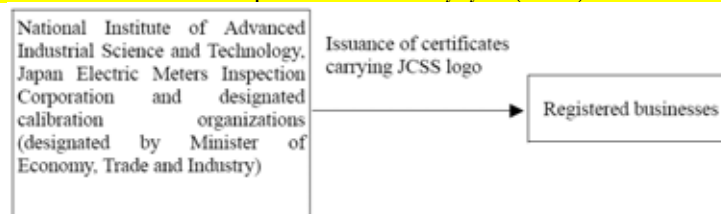
3 How to cope with

- 1) Establishment of traceability by Japan Calibration Service System (JCSS)
- 2) Acquisition of ISO 17025 accreditation to establish better management system
- 3) Acquisition of the accredited specified measurement certification business to measure trace of dioxins
- 4) Review of the current accuracy management
- 5) Consideration of re-education system of the certified environmental analyst
- 6) Participation of technical skill test for measurers

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Schematic Representation of Traceability System (JETRO)



Calibration using specified standards (direct calibration through national measurement standards (JETRO))

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Accuracy management in environmental measurement

1 Internal accuracy management

- 1) Preparation of kinds of rules, standard operation procedure (SOP) and kinds of records
 - ◆ Handling of equipment
 - ◆ Handling of standard
 - ◆ Sampling
 - ◆ Pre-treatment
 - ◆ Handling of measurement instruments
 - ◆ Recoding of each analysis process
- 2) Periodic acquisition of data for validation of accuracy management in analysis
 - ◆ Limit of detection value (LOD) of measurement instrument and analysis method: once a year
 - ◆ Recovery rate evaluation: 80 -120 %
 - ◆ Operational blank and travel blank test.
 - ◆ Repeated measurement: Differences are less than 20 % (The figure depends on the method) of the average. to be executed approximately 10 % of the number of samples.

2 External accuracy management by cross-check, participation to skill evaluation tests, etc

- ◆ Confirmation of measurement reliability
- ◆ Establishment of measurement value
- ◆ Improvement and confirmation of measurement skill of the measurer

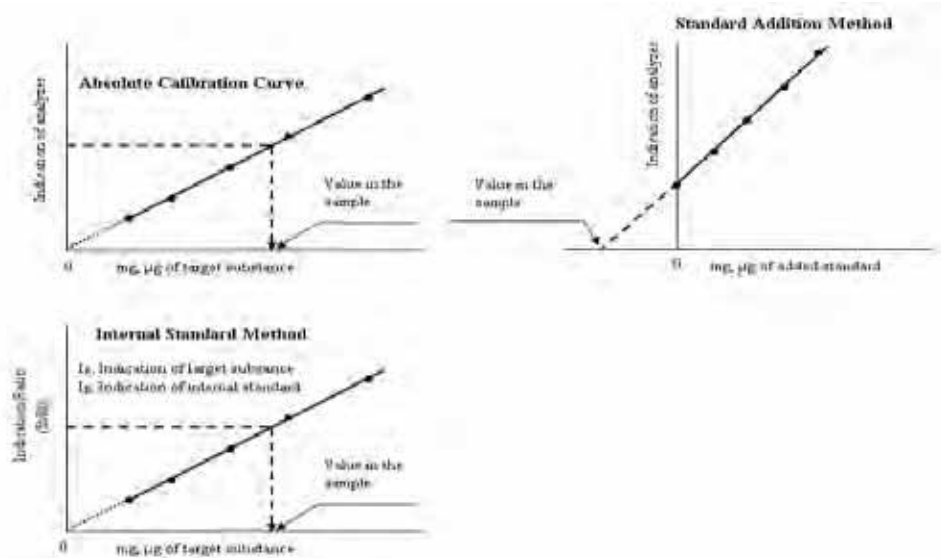
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Attention in using measurement instruments

Measurement Instrument	What to be paid attention to
Spectrophotometer	<ul style="list-style-type: none"> ◆ Understand the principal of analysis procedure ◆ Understand coloring agents with other elements ◆ Adjust pH to the appropriate range ◆ Add buffer, masking, reaction agents as designated ◆ Appropriate pre-treatment such as distillation, solvent extraction, etc ◆ Reaction temperature ◆ Right wave length ◆ Blank test
Flame atomic Absorption Spectrophotometer	<ul style="list-style-type: none"> ◆ Understand spectrometric, physical and chemical interferences and countermeasures ◆ Use background correction, solvent extraction, interference restriction agent, etc ◆ Use high temperature flame as designated ◆ Use internal standard method calibration curve ◆ Procedure of ignition and stop of flame ◆ Blank test
Electric heating atomic Absorption Spectrophotometer	<ul style="list-style-type: none"> ◆ Use background correction for Al, Cr, V ◆ Use Palladium(II) nitrate for Cd, Pb to avoid element loss in ashing process ◆ Use solvent extraction if necessary ◆ Repeat measurement at least three times ◆ Blank test
Inductively Coupled Plasma (ICP) atomic emission spectrometry	<ul style="list-style-type: none"> ◆ Use standard addition or internal standard calibration curve ◆ Use solvent extraction if necessary ◆ Blank test
Ion selective electrode	<ul style="list-style-type: none"> ◆ Temperature ◆ Measurement time to become stable ◆ pH adjustment ◆ Pre-treatment by adding complex-dissolving agent to change to ionic-form, distillation, adding masking agent, etc.

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Calibration Curve



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Attentions in Measurement

Parameter	What to be paid attention to
pH	<ul style="list-style-type: none"> ◆ Glass and reference electrodes are stored in water. ◆ If they are dirty, clean in a short time by dilute HCl or surfactant and wash by water flow ◆ Add KCl for reference electrode if necessary ◆ Temperature ◆ Use lithium electrode for the sample with high pH (over pH 11).
Biochemical oxygen demand (BOD ₅)	<ul style="list-style-type: none"> ◆ Check pH, oxidation or reduction agent, supersaturated dissolved oxygen or gas ◆ Pre-treatment above if necessary ◆ Use seed liquid ◆ Use the result where D.O in the incubator is consumed 40 to 70 % in five days ◆ Check the total procedure by using Glucose-Glutamine mixture standard liquid to show 220±10 mg-O/L ◆ Understanding of the advantages and disadvantages of DO measurement methods by titration
Dissolved oxygen (D.O) meter	<ul style="list-style-type: none"> ◆ Temperature and salt concentration ◆ Keep the electrode clean and wet
Conductivity meter	<ul style="list-style-type: none"> ◆ Temperature ◆ Keep the cell clean and wet ◆ Need a certain flow rate
Chemical oxygen demand (COD _{Mn})	<ul style="list-style-type: none"> ◆ Water bath : to keep over 93 °C during the test ◆ Shape of triangle flask : same ◆ Cl⁻ concentration ◆ Use the result where KMnO₂ solution remains 4.5 to 6.5 mL.
Chemical oxygen demand (COD _C)	<ul style="list-style-type: none"> ◆ Take sample as half of K₂Cr₂O₇ remains ◆ Reagents concentrations ◆ Cl⁻ concentration: Not appropriate to the sample with less than 20 mg-O/mL and high concentration of Cl⁻
Suspended Solid (SS) under 2 mm	<ul style="list-style-type: none"> ◆ Take sample as more than 5 mg of dries SS remained. Preferably 20 to 40 mg. ◆ Heating temperature and time
n-hexane extracted substances	<ul style="list-style-type: none"> ◆ Not use grease on the cock of the separation flask with short leg ◆ Check the nature of the extracted substances such as emulsion, turbidity, etc. Consider to use soxhlet extractor.

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Attentions in Measurement

Parameter	What to be paid attention to
Pre-treatment of analysis of heavy metals	<ul style="list-style-type: none"> ◆ Understand the applications of dissolving procedures of metals by acids ◆ Don't use HNO₃-H₂SO₄ when use AA or ICP and Pb ◆ Understand the advantages and disadvantages of evaporation concentration, co-sedimentation, vaporizing, ion-exchange, solvent extraction, etc.
Cu, Zn, Pb, Cd, Mn, Fe, Ni, Co by AA or ICP	<ul style="list-style-type: none"> ◆ Use solvent extraction, if necessary. Use background correction ◆ Avoid contamination from glass apparatus and environment ◆ Prepare of mixed standard solutions of Zn, Pb, Cd, Mn, Fe, Ni, Co for calibration curve in using ICP
Cr	<ul style="list-style-type: none"> ◆ Concentrate by co-sedimentation, solvent extraction in case of low concentration of Cr
Phenols (Distillation, Spectrophotometer)	<ul style="list-style-type: none"> ◆ Pre-treatment: distillation ◆ Understand the meanings of the added reagents ◆ pH at reaction with reaction agent, reaction time, temperature
T-N (Oxidation, ultra violet Spectrophotometer)	<ul style="list-style-type: none"> ◆ Pre-treatment: oxidation at high temperature and high pressure by oxidation agent ◆ Not suitable for the sample with high concentration of organic matters, seawater, sample with more than 1mg/L of Cr ◆ In case of the existence of high concentration of organic matters, use total amount nitrogen method
T-P (Oxidation, visible Spectrophotometer)	<ul style="list-style-type: none"> ◆ Pre-treatment: oxidation at high temperature and high pressure by oxidation agent ◆ Understand the limit of the application of the sample, not suitable for the sample with high concentration of organic matters. Cl, etc.
Common	<ul style="list-style-type: none"> ◆ Grade of pure water

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Classification and Required Quality of Pure Water

Parameter ^{*1}	Classification and required quality			
	A1	A2	A3	A4
Conductivity (mS/m at 25 °C)	Less than 0.5	Less than 0.1 ^{*2*}	Less than 0.1 ^{*2}	Less than 0.1 ^{*2}
TOC (mg/l)	Less than 1	Less than 0.5	Less than 0.2	Less than 0.05
Zn (μg/l)	Less than 0.5	Less than 0.1	Less than 0.1	Less than 0.1
SiO ₂ (μg/l)	-	Less than 50	Less than 5.0	Less than 2.5
Cl (μg/l)	Less than 10	Less than 2	Less than 1	Less than 1
SO ₄ ²⁻ (μg/l)	Less than 10	Less than 2	Less than 1	Less than 1

Note

- *1 Parameters may be selected by analysis method. If there is the criterion on the water to be used in the analysis method, follow it.
- *2 The value of effluent from water purification equipment by direct introduction of it to the detector of conductivity meter
- *3 In case of direct introduction of the effluent from membrane equipment after final ion-exchange equipment to the detector of conductivity meter, the value should be less than 0.01 mS/m at 25 °C

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What to be paid attention to in analysis of industrial wastewater (Additional)

1 BOD₅

- ◆ When TDS exceeds 3,000 mg/L in incubation bottle, the BOD₅ value extremely becomes low because of high level of salt hinders bacteria's activity.
- ◆ Number of bacteria in incubation bottle needs at least 10⁵cfu/ml. Accordingly, filtered by membrane needs seeding for analysis of BOD₅ because bacteria are also filtered by the membrane.
- ◆ Seeding will be always necessary.
- ◆ Add the seed liquid so that BOD₅ of the seeded dilution water becomes 0.6 to 1.0 mg-O/l (by calculation of BOD₅ of seed liquid itself)
- ◆ When BOD₅ value of standard solution does not show 220±10 mg-O/l, the procedure should be reviewed.
- ◆ Analyze DO1 (DO of first day) 15 minutes after preparation of sample du to prevent inorganic reduction agent from consuming oxygen.
- ◆ DO discrepancy during five days in incubator bottle should be 0.2 mg-O/l or less.
- ◆ Starch indicator should be prepared just before titration.

34

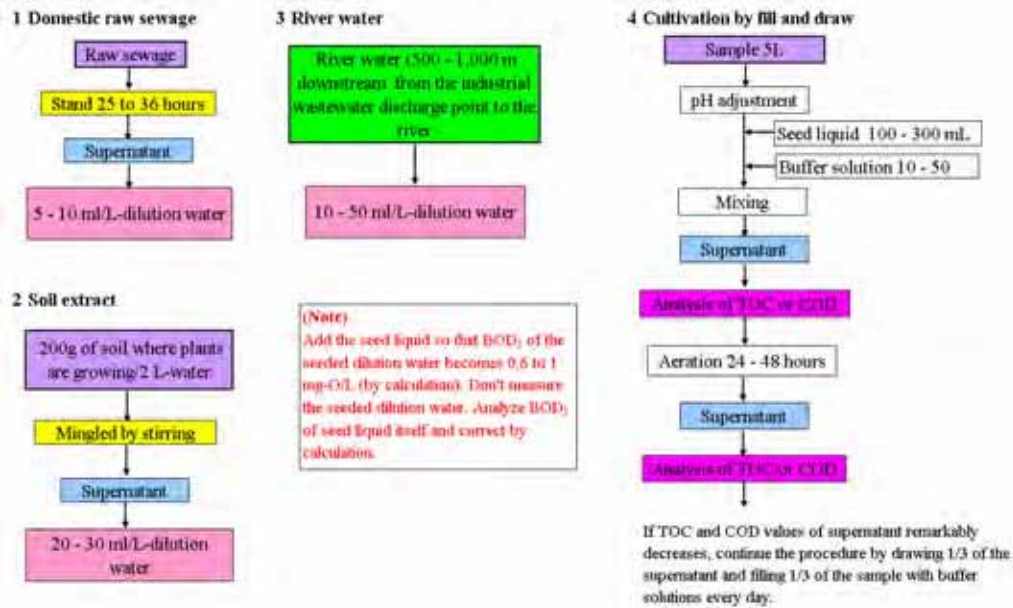
What to be paid attention to in analysis of industrial wastewater (Additional)

2 General

- ◆ Preparation of calibration curve
- ◆ There is a range of calibration curve. Don't use the lower and upper value of the calibration curve.
- ◆ Understanding of the importance of pre-treatment, in using spectrophotometer, particular, and even in using AA, ICP, Gas chromatography
- ◆ Confirmation of recovery rate of extraction, distillation operation, etc.
- ◆ Effective time of prepared agents, standards and indicators.
- ◆ Blank test
- ◆ Cleaning of beaker, flask, extraction and/or distillation apparatus, measurement instruments, etc to prevent from contamination
- ◆ Error among the cell for spectrophotometer
- ◆ How to distribute the sample with suspended solid
- ◆ Stability of the measurement instruments before measuring
- ◆ Understanding of the meaning of the significant figure and decision
- ◆ Preparation of analysis flowchart with remarks

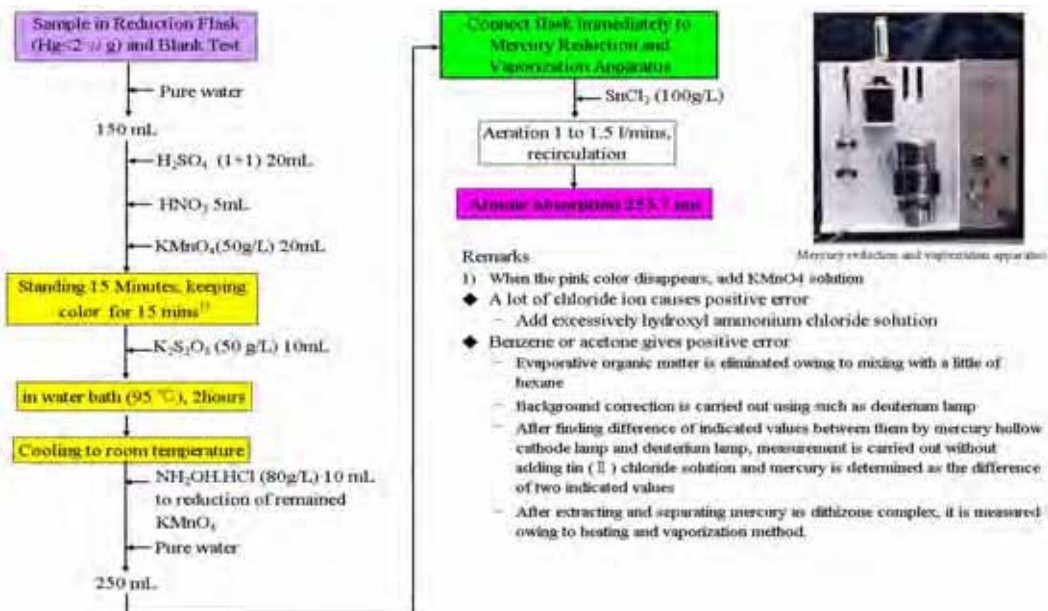
35

Preparation of Seed Liquid



36

An Example of Analytical Flowchart (Hg)



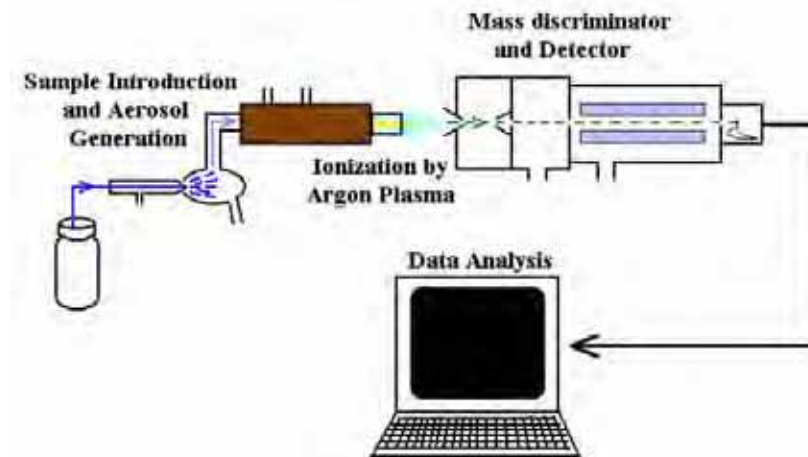
Mercury reduction and vaporization apparatus

37

Recommendations

- ◆ Don't end up only analyzing and measuring. Use the results for plant operation, consultation, etc. When the results are not what you expected, you should pursue the causes and consider the procedures to improve.
- ◆ Find the correlation among the parameters to use daily operation & maintenance, BOD₅-COD_{cr}-SS, for example. If you find the correlation, you don't need analyze all parameters every time. Formulate a database from the results.
- ◆ In case of using simple analysis method, not official, compare the results with the one got by official method. If there is no co-relation, don't use the simple method. It only causes the confusion.
- ◆ During analysis, you should pay attention to if there is an unusual phenomenon, for example, in color, generation of turbidity or settlements and so on. This abnormality will give you some hints in the trouble of the plant and analysis procedure. Analysis or measurement is not a routine work.

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Schematic flow of ICP-MS by Jenna Worley and Steve Kvech

Thank you for your attention. See you again

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3.1.4 Industrial wastewater treatment



Industrial Wastewater Management -3 Industrial Wastewater Treatment



16 October 2008, IZAWA Tetsuo

1



Topics of This Seminar

- Planning of Wastewater Treatment
- Countermeasures to reduce wastewater generation and pollution load
- Selection of Treatment Process by Experiment
- Flow measurement
- Biological Treatment
- Treatment of Hazardous Substances
- Analysis of Hazardous Substances
- Sludge Treatment for reuse, recycle
- Others

2

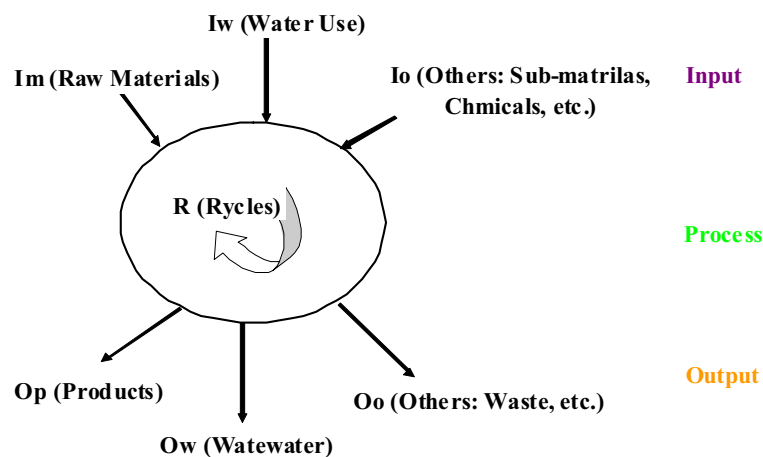
Planning of Wastewater Treatment

What to be studied for Planning Wastewater Treatment

- ◆ Quantity and quality of industrial wastewater
 - Existing factory : Actual measurement
 - New Factory : Estimation from the existing data, etc from similar factories
 - : Estimation from water balance by each production process and material balance
- ◆ Water quantity and quality of the upper and down streams of the river where wastewater is to be discharged to
- ◆ Environmental criteria of the river, sea or lake to be discharged to
- ◆ Situation of water use
- ◆ Creatures living in water body
- ◆ Expansion of the factory and increase of production,
- ◆ Trend of water pollution regulation both by central and local government,
- ◆ People's feelings,
- ◆ Rationalization of water use, change of production process or facilities, if necessary

3

Concept of Material Balance



4

Countermeasures to reduce wastewater generation and pollution load

The principal of wastewater treatment is to reduce wastewater and pollution as much as possible **by the appropriate process control.**

- 1) To reduce raw materials (Im)
 - ◆ To use cleaned raw materials
 - ◆ To shift the raw materials with better quality and yield
- 2) To reduce sub-materials and chemicals, etc. (Io).
 - ◆ To shift the alternatives with lower load
 - ◆ To use appropriate quantity
- 3) The counter measures in production process
 - ◆ To shift the part of loads in wastewater to product (Op) or Waste, etc.(Ow)
 - ◆ To reduce the materials, etc. (Im) and Water use (Iw) by recycle



Water Saving Tap

5

Countermeasures to reduce wastewater generation and pollution load

Concretely

1) Segregation of wastewater:

- ◆ Production wastewater, cooling water, sanitary wastewater
- ◆ In case of separation of water and insoluble substances such as hydroxides or sulfides of heavy metals, concentrated wastewater is preferable.
- ◆ Wastewaters with cyanide and chromium compounds are separated to treat in plating factory.
- ◆ In case of biological treatment of organic wastewater, wastewater with hazardous or high or low pH should not be mixed.
- ◆ In the public water body with severe limitation of discharging n-hexane extraction substances (oil), wastewater including soluble oil should not be mixed with other wastewater.

2) Water savings:

- ◆ Adopting counter flow cleaning.

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Countermeasures to reduce wastewater generation and pollution load

3) Change of production process: advanced process control; improvement of facilities, change or improvement of raw materials; Inspection of facilities and equipment, etc.

- ◆ Replacement of starch to CMC (Carboxymethylcellulose) : textile industry
- ◆ Development of non- electrolysis method (chemical plating) without using cyanide: plating industry
- ◆ Reduction of scooping of plating liquid between plating tank and water washing tank: plating industry
- ◆ Installation of oil trap at each process: oil refinery industry
- ◆ Recovery of chemicals from delignification wastewater (Black liquid) in paper manufacturing factory
- ◆ Recovery of chromium acid from plating wastewater

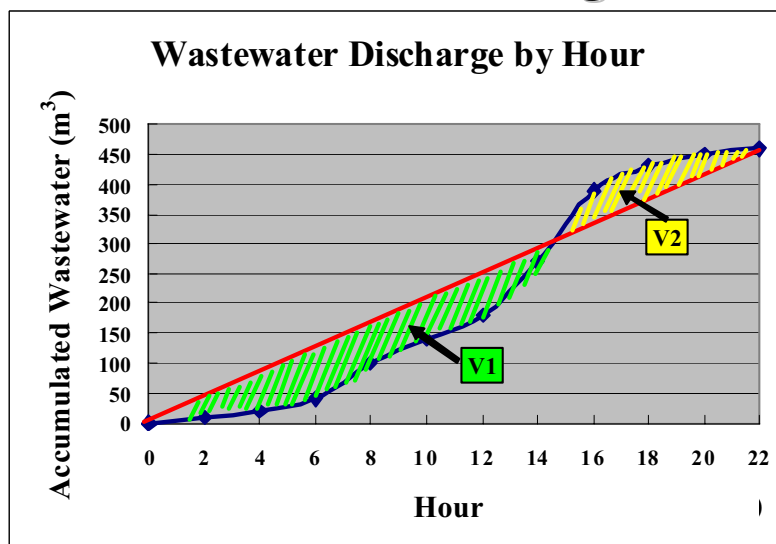
4) To average wastewater quality and quantity

5) Monitoring of wastewater system

- ◆ Alarm system
- ◆ Monitoring main pollutant generation process

7

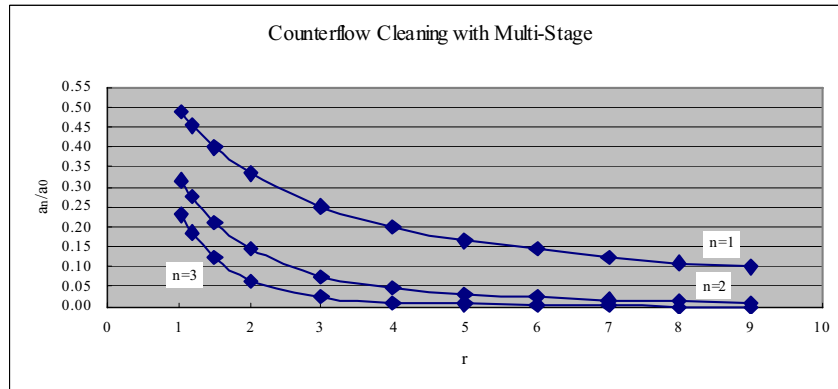
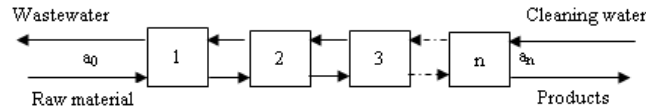
To Make Average



Necessary Tank Volume to Make Average = $V1+V2$

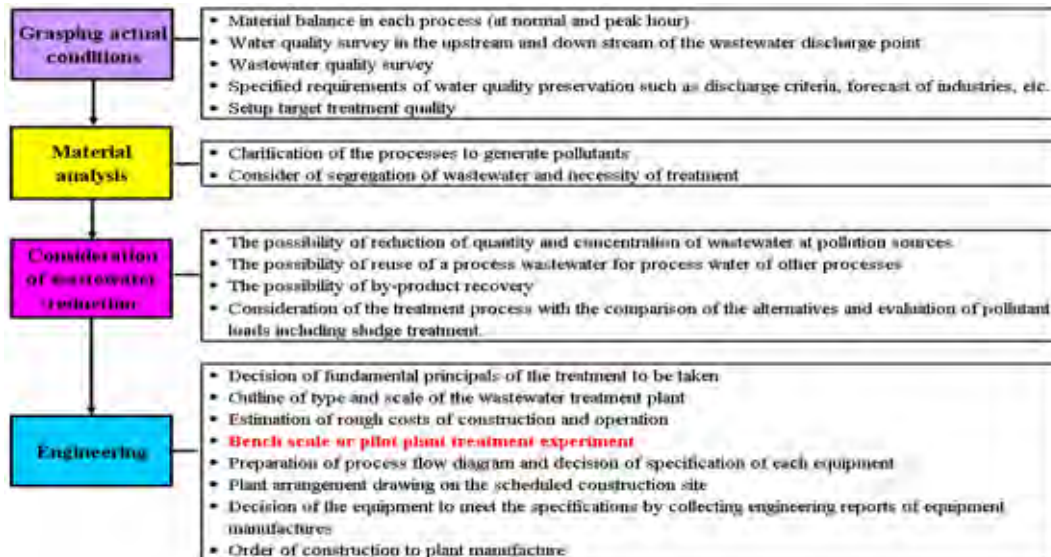
8

Counter Flow Cleaning



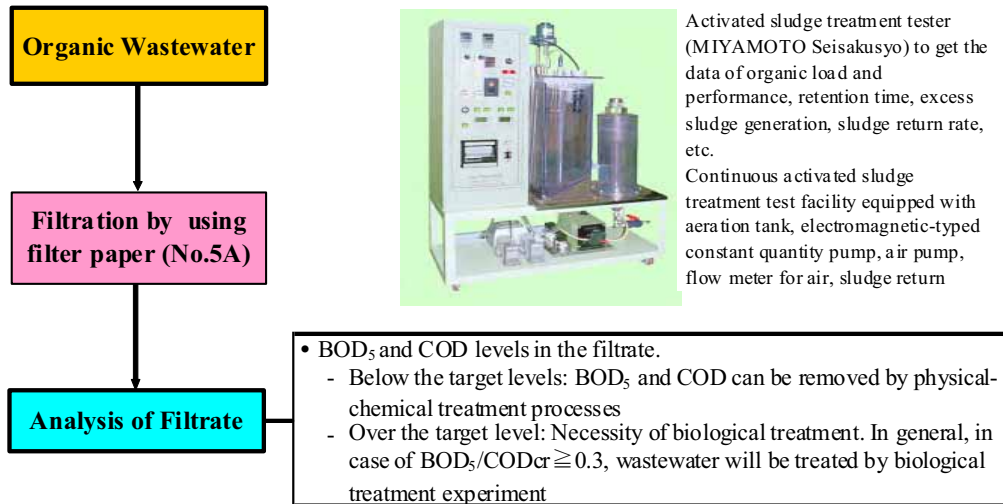
9

Study Procedures of Wastewater Treatment Plan



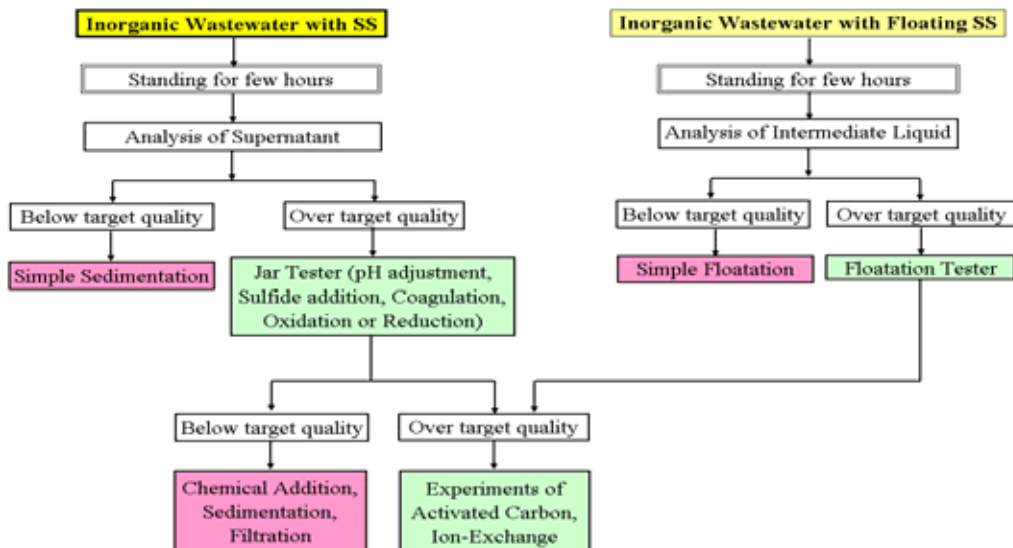
10

Selection of Treatment Process by Experiment



11

Selection of inorganic wastewater treatment process



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Selection of Treatment Process by Experiment



Water Treatment Experiment Equipment

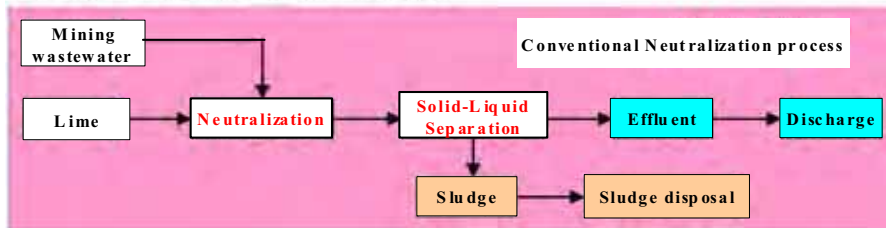
13

Selection of Treatment Plant Type

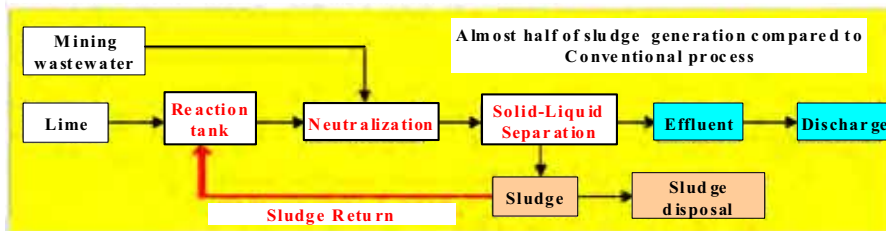
- **Treatment capacity**
- **Installation area**
- **Construction and operation costs such as power, chemicals, labor, etc.**
- **Easiness of operation and maintenance**
- **Quantity of sludge generation and easiness of sludge treatment**
- **Reliability of the manufacture (technical capability, after service and achievements, etc.)**

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Improvement of concentration of metal hydroxide by neutralization



Conventional Neutralization Process



Sludge Return Neutralization Process (HDS: High Density Solids Method)

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Flow Measurement

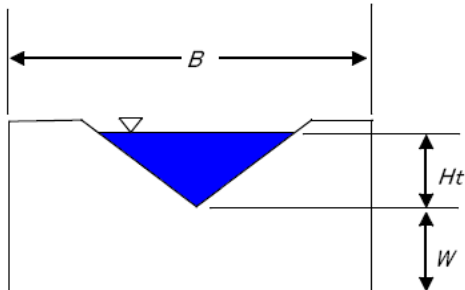
1. Measurement by Container
2. Measurement by Weir-Open Channel

	Weir type	Flume type
Instruments	Triangle, rectangular, or full width weir and level meter	Partial flume and level meter
Principal	To measure upstream level to overflow by installing weir plate in the course of open channel	To measure upstream level by lessening the part of width of the channel (throat)
Measurement range	0.02~10 m ³ /s	0.002~2.5 m ³ /s
Head loss	0.3~0.6 m	Less than 0.2 m in general
Necessary length of straight line of channel	Upstream 4 to 5 times of weir width	Upstream 4 to 5 times of weir width of throat
Accuracy	roughly ±4%	roughly ±4%
Advantage and disadvantage	Simple structure, small cost	Almost no accumulation of solids.
	Accumulation of solids at upstream	Large scale and complicated shape

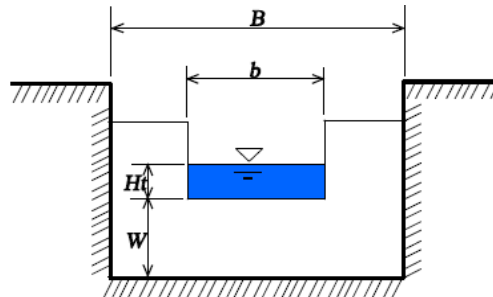
Prepare the relation figure of head loss (water level) and flow rate.

16

Triangle and Rectangle Weir



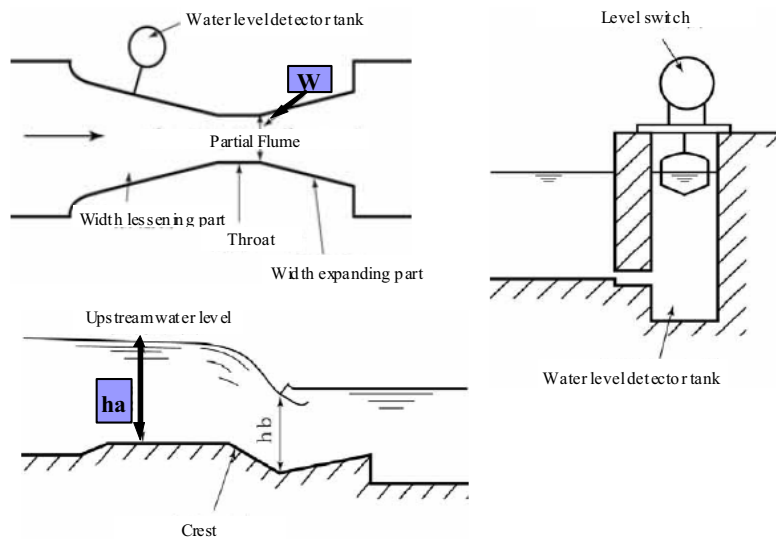
Triangle weir $Q = C Ht^{5/2}$ (m^3/s) at 90 degree triangle weir



Rectangle weir $Q = CbHt^{3/2}$ (m^3/s)
Flow rate is proportional to Ht and C (Flow rate coefficient) is calculated by B , b , W and Ht .

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Partial Flume



Partial Flume $Q = K \cdot h_a \cdot m$
 Q : Flow rate (m^3/h), h_a : Upstream water depth (m)
 K , m : Constant decided by shape, size and throat width of the flume

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Flow Meter for Pipe-1

	Electromagnetic type	Orifice type	Venturi type	Ultrasonic type	Vortex type	Impeller type
Instruments	Electromagnetic meter	Orifice plate and differential pressure meter	Venturi tube and differential pressure meter	Ultrasonic flow meter	Vortex meter	Impeller flow meter
Principal	A voltage is induced when a conductor (liquid) moves through a magnetic field. The amount of voltage produced is directly proportional to the flow rate.	Putting a plate with a hole in the tube causes differential pressure at the front and the rear of the plate. The differential pressure has a relation with flow rate.	Same as orifice meter, using venturi tube in place of orifice.	The configuration is such that the sound waves travelling between the devices are at a 45 deg. angle to the direction of liquid flow. The speed of the signal travelling between the transducers increases or decreases with the direction of transmission and the velocity of the liquid being measured. A time differential relationship proportional to the flow can be obtained by transmitting the signal alternately in both directions.	When a liquid flows around a bluff object, eddies or vortices are shed alternately downstream of the object. The frequency of the vortex shedding is directly proportional to the velocity of the liquid flowing through the meter.	The rotor spins as the liquid passes through the blades. The rotational speed is a direct function of flow rate.

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Flow Meter for Pipe-2

	Electromagnetic type	Orifice type	Venturi type	Ultrasonic type	Vortex type	Impeller type
Tube size to be applied	2.5 to 3,000 mm	15 to 3,000 mm	50 to 1,200 mm	25 to 3,000 mm	25 to 200 mm	50 to 400 mm
Pressure loss	No	25 to 80 % of differential pressure	5 to 20 % of differential pressure	No	Small	Small
Necessary length of straight pipe (to inner pipe size of the flow meter)	Upstream about 5D	Upstream 10 to 50 D, Downstream 4 to 8D	Upstream 1 to 4.5 D, Downstream 4 times of throat diameter	Upstream 10 to 50 D, Downstream 5D	Upstream 10 to 50 D, Downstream 5D	Upstream 10 to 50 D, Downstream 3D
Influence of solids	No	Yes	Yes	Yes	Relatively small	Yes (Need strainer)
Rough accuracy (%)	± 0.5 to 1.0	± 2 to 3	± 2 to 3	± 1 to 1.5	± 1	± 2 to 4
Remarks	Not used for the liquid without electricity conductivity	Clogging and pressure drop by orifice causes easily troubles	Same as orifice type	-	-	-

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Flow measurement-Open Channel

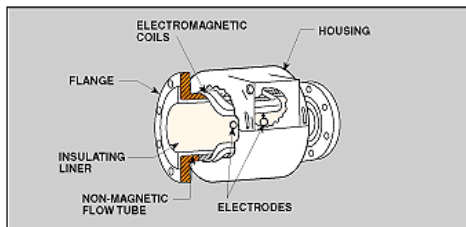


ONE-P
Measurement method: Time-Distance
Sensor: Ultrasonic Flow Meter
Applicable level: 0.15-2 m
(Pentough Corporation)

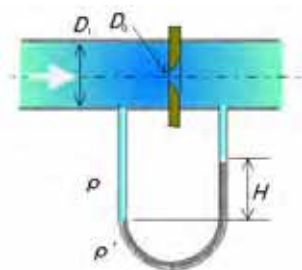
MS-P II
Measurement method: Level-Flow Automatic Calculation
Sensor: Ultrasonic Flow Distribution Sensor
(Pentough Corporation)

21

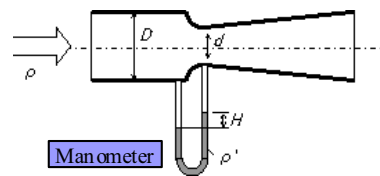
Figures of Flow Meters for Pipe-1



Magnetic Flow Meter



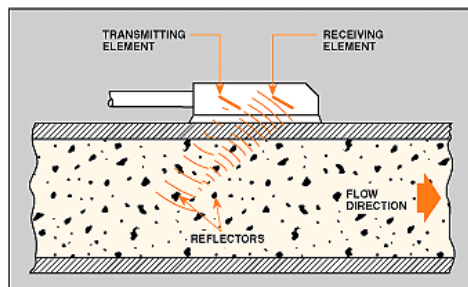
Orifice Flow Meter



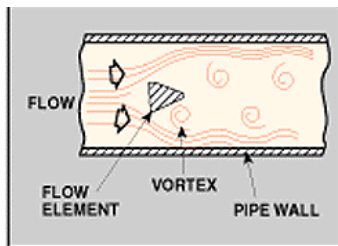
Venturi Flow Meter

22

Figures of Flow Meters for Pipe-2



Ultra Sonic Flow Meter



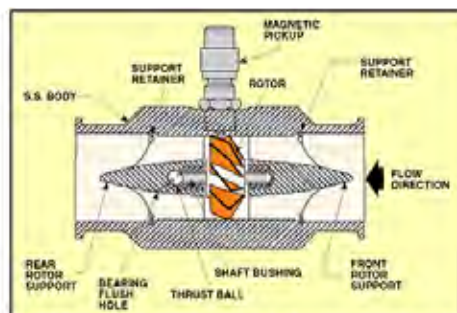
Vortex Flow Meter

23

Flow Meter for Pipe-3



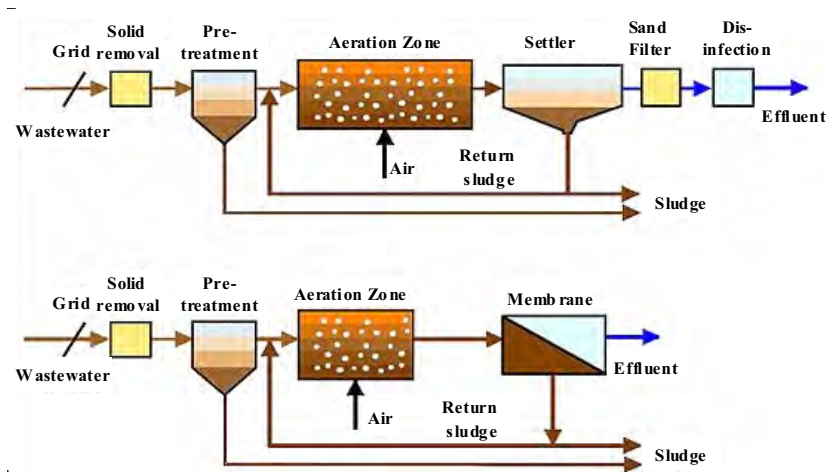
Potable Flow Meter
(Ultra Sonic Flow Meter)



Turbine flow meter
(Seil Enterprise Co.)

24

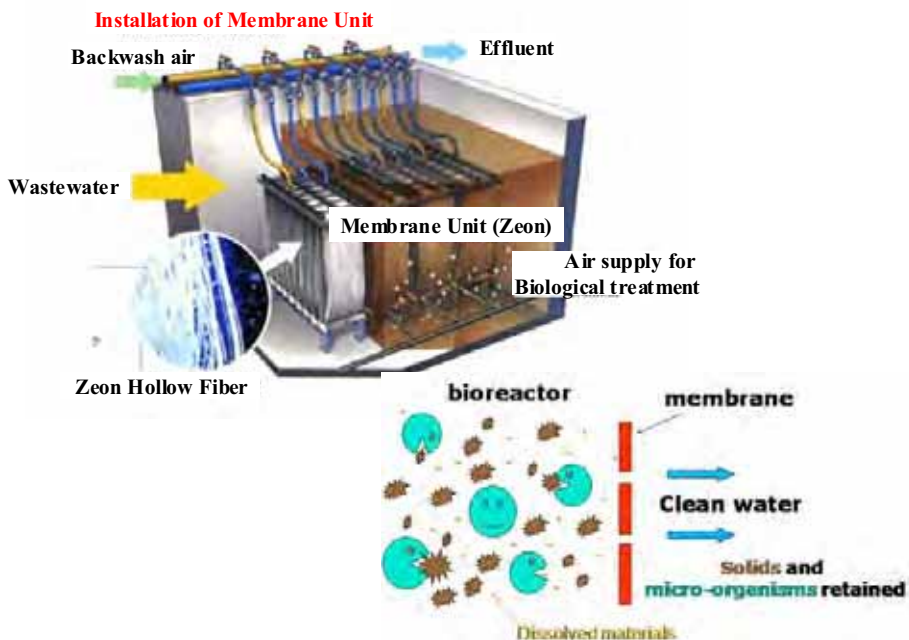
Wastewater Treatment-1



Schematic of conventional activated sludge process (top) and membrane bioreactor (bottom)

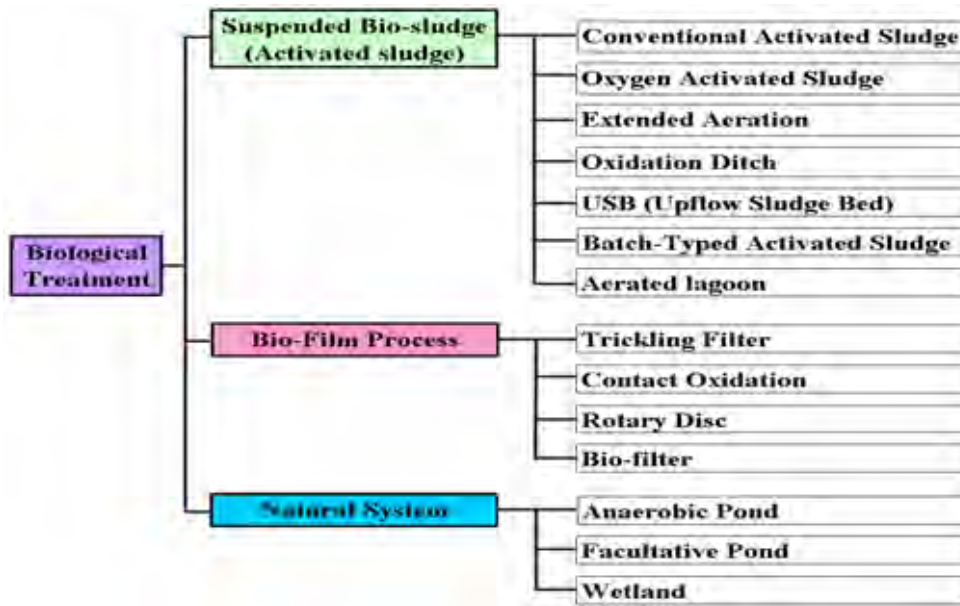
25

Membrane Bioreactor



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Biological Treatment



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Characteristics of Biological Treatment

	Suspended bio-sludge system	Bio-film system	Natural pond system
Principal	Flock of microbe called activated sludge is suspended in a reactor. Suspended sludge has functions of adsorption, oxidation/reduction and decomposition of organic matter in terms of BOD ₅ or/and parts of COD	Microbes attached and thrived on the surface of media such as plastic, stone, sand, honeycombed type cell, fiber and so on. Adsorb, oxidize/reduces and decompose organic matters in terms of BOD ₅ and parts of COD	Microbes naturally thrived in the natural pond oxidize/reduces and decompose organic matters in terms of BOD ₅ and parts of COD
Advantage	<ul style="list-style-type: none"> When solid-liquid separation is properly achieved, clear treated water can be obtained. 	<ul style="list-style-type: none"> Not necessary of control of sludge return Relatively easy maintenance Relatively strong for fluctuation of quality No need final sedimentation tank in bio-filter method Smaller space than suspended bio-sludge system 	<ul style="list-style-type: none"> No need power Easy maintenance Maintenance cost is minimum.. Possible to remove N and P Strong to quantity fluctuation Hygienic bacterial removal by increasing numbers of ponds

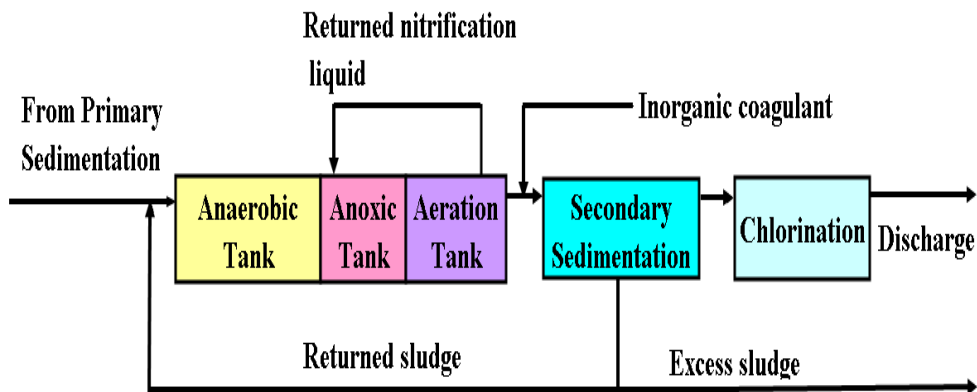
28

Characteristics of Biological Treatment

	Suspended bio-sludge system	Bio-film system	Natural pond system
Disadvantage	<ul style="list-style-type: none"> ♦ Solid (activated sludge) - liquid separation and keeping sludge concentration in the reactor by returning concentrated sludge from sedimentation tank are the key factors. ♦ Need trained and skilled technicians ♦ USB and conventional activated sludge method are weak in fluctuation of quality. 	<ul style="list-style-type: none"> ♦ Impossible to control microbes due to no sludge return. ♦ Generally the final effluent is not clear due to flow out of small particle of microbe 	<ul style="list-style-type: none"> ♦ Need large space

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Removal of Nitrification and Phosphorus by Biological Treatment



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Characteristics of Removal of Nitrogen and Phosphorus by Biological Treatment

1) Principal

- ◆ Three (3) reactors in series
- ◆ Phosphorus removal: by excess intake of phosphorus by activated sludge
- ◆ Nitrogen removal: Nitrification in aeration tank and de-nitrification in anoxic tank

2) Features of the process

(Advantages)

- Removal rate of nitrogen and phosphorus is 60-70 and 70 -80 %, respectively.
- Removal rate of organic matter is superior to conventional activated sludge process
- Few chances of occurrence of bulking of activated sludge

(Disadvantages)

- 1.5 to 2 times of space is necessary compared to conventional activated sludge process
- Re-dissolution of phosphorus in anaerobic sludge treatment
- Phosphorus removal limitation
- Al or Fe coagulant is used to highly remove phosphorus

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Performance Evaluation

1) Setting target level: BOD₅ 10 mg/L, SS 20 mg/L, T-N 10 mg/L, T-P 1.0 mg/L

2) Factors to influence on performance

- ◆ Inlet quality of BOD₅, SS, N and P and flow rate
- ◆ Water temperature
- ◆ pH
- ◆ MLVSS, SRT, A-SRT (aerobic sludge retention time) in the reactors
- ◆ HRT of each biological tank
- ◆ ORPs of anaerobic and anoxic tank
- ◆ DO of aeration tank
- ◆ Return load from sludge treatment process

3) Notes

- ◆ Hourly and daily fluctuation, install automatic meters with recording
- ◆ Correlation of automatic analysis equipment such as pH meter, MLDO meter, MLSS meter, ORP meter, COD meter with official analysis methods
- ◆ Biological Activity Check
- ◆ Qualitative evaluations of air supply, excess sludge generation, sludge return rate, Dynamic simulation formula of MLSS-Temperature, inlet and outlet quality, etc.

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Quality Monitoring

	Inlet of Anaerobic Tank	Outlet of Anaerobic tank	Outlet of Anoxic Tank	Outlet of Aerobic Tank	Outlet of secondary clarifier	Returned sludge
pH	○			○☆	○	○
MLDO				○☆		
MLSS			○	■☆		
SV				○		○
ORP		☆	☆			
NH ₄ -N	●◎■	●◎■	●◎■	○●◎■	○●◎■	
NOx-N	●◎■	●◎■	●◎■		○●◎■	
Org-N	●◎■				●◎■	
T-N	●◎■☆				●◎■☆	
S-PO ₄ -P	●◎■	●◎■	●◎■	○●◎■	○●◎■	
T-P	●◎■☆				●◎■☆	
Alkanity	●◎■			■	●◎■	
SS	○◎●				○◎●	○
BOD ₅	●◎■				●◎■	
S-BOD ₅	●◎■				●◎■	
COD	●◎■☆				●◎■☆	
S-COD	●◎■☆				●◎■☆	
DO	○				○	○
Temperature	○◎●				○◎●	
Transparency	○◎●				○◎●	

(Remarks)

○: Daily check

●: Regular check

◎: Check though the day

■: Biological activity check

☆: by Automatic meter

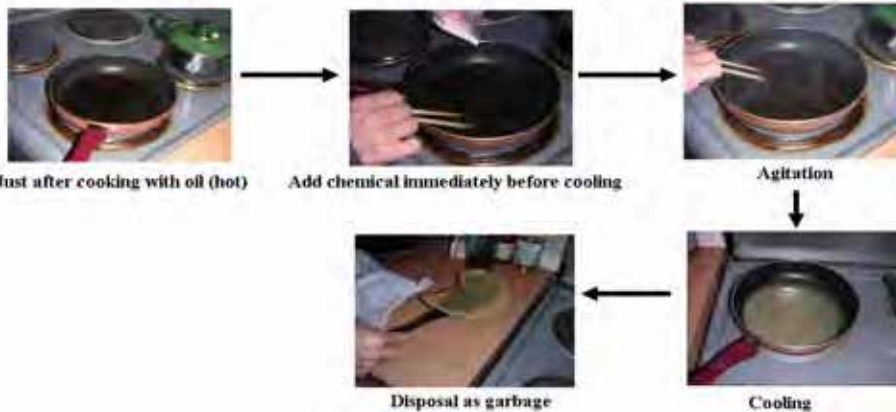
NOx-N: NO₃-N + NO₂-N

Analysis Method: by sewage analysis method

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Why entering oil/grease to the WWTP is restricted?

- ◆ Clog the sewer
- ◆ Negative effect on the performance of clarifier
- ◆ Negative effect on oxygen supply in aeration tank
- ◆ When it turns to acid by bacteria activity in sewer, BOD₅ value increases drastically. It means the load of the plant increases drastically to the extent of the limit of design level and the effluent performance becomes worse, even with mechanically



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Treatment of Heavy Metals-1

- 1) **Hydroxide method**
 - ◆ Lime is better in terms of nature of dehydration.
- 2) **Co-precipitation**
 - ◆ Ferrous or ferric chloride or sulfate is used as iron salt. Sulfate salt is superior to chloride salt in the nature of dehydration.
- 3) **Crystallization-typed neutralization**
 - ◆ Reactor type packed with seed crystallization or sludge recirculation process is applied.
 - ◆ Fluorine is removed up to 10 to 20 mg/l and around 8 mg/l by conventional neutralization and crystallization-typed neutralization, respectively.
- 4) **Ion reaction**
 - ◆ Antimony (SbO_4^{3-}), molybdenum (MoO_4^{2-}), tungsten (WO_4^{2-}) etc. formulate insoluble salt with iron salt.
 - ◆ $\text{Fe}^{3+} + \text{AsO}_4^{3-} \rightarrow \text{FeAsO}_4 \downarrow$
- 5) **Peculiar Reaction**
 - ◆ Ammonia complexes of zinc, copper, nickel, cadmium, etc which hardly formulate hydroxides by conventional method formulate hydroxide with the existence of Cr^{3+} .
- 6) **Substitution method**
 - ◆ In general, wastewater including metals can't remove by simple pH adjustment because it also includes **chelating agents and/or dispersion agents**.
 - ◆ It is important to make the average to lessen the concentration of chelating agents or separate concentrated such wastewater.
 - ◆ Mg salt or Fe + Ca salt is used. The former has superior effects on sludge reduction and COD absorption; however, the later is used generally.

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Treatment of Heavy Metals-2

- 7) **Sulfide Process**
 - ◆ The application of this process has been very limited, only for mercury treatment, due to the toxicity, intense odor and the nature of erosion of hydrogen sulfide.
 - ◆ Excess sulfide is necessary to form a complete sulfide compounds.
 - ◆ Further excess sulfide brings re-dissolution.
 - ◆ Generally iron salt is added for the reaction with the excess sulfide and improvement the coagulation effect by co-precipitation effect.
 - ◆ Recently **special sulfurous heavy metal fixing agent** is used.
 - ◆ However, **pre-treatment test is necessary** depending on kind and concentration of the complex like for EDTA complex **with nickel or chromium**.
 - ◆ In case where a different nature complex like **organic acid complex** such as oxycarbonic acid or carbonic acid complex and ammonia complex exists, treatment along with substitution method may be necessary.
 - ◆ For the segregated wastewater including kinds of chelating agents such as EDTA, citric acid with mercury, cadmium, cyanide, etc **from laboratories of a university**, this method can't remove mercury and cadmium due to the effect of chelating agents.
 - ◆ Here, this method is adapted after **decomposition of cyanide and chelating agents** such as EDTA, citric acid, etc **by alkali chlorine decomposition by adding nickel salt**. It is possible to decompose the chelating agents such as EDTA, citric acid, etc by heat decomposition by **KMnO₄ (potassium permanganate) or fenton method** using Hydrogen peroxide and iron salt.

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Treatment of Heavy Metals-3

8) Ferrite process

- ◆ Mixing the solution containing ferrous ion with caustic soda at the rate of $2\text{NaOH}/\text{FeSO}_4=1$ at more than $60\text{ }^\circ\text{C}$ to make the solution of more than pH 9 forms ferrite, a strong magnetic body, (Magnetite: $\text{MO}/\text{Fe}_2\text{O}_3$ (M: Fe, Co, Mn, Ni, Cu, Mg, Zn, Cd, etc).
- ◆ Advantages
 - Possible to treat kinds of metals simultaneously
 - Metals in the crystal structure of ferrite are hard to dissolved
 - Suitable for small sized wastewater treatment such as from laboratories containing kinds of heavy metals
- ◆ Disadvantages
 - Mercury treatment from exhaust gas because mercury in wastewater moves into exhaust gas
 - Chelating agents such as EDTA, organic acid, etc should be treated by oxidation decomposition process in advance
 - A lot of sludge generation

9) Iron powder method

- ◆ This method is to precipitate co-existing ion by the difference of ionization tendency.
- ◆ Scrap iron is used to recover copper in mining wastewater.
- ◆ Dissolved iron ion has the function of co-precipitation.
- ◆ $\text{Fe}^0 + \text{Cu}^{2+} \rightarrow \text{Fe}^{2+} + \text{Cu}^0$ (pH 2-4)

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Treatment of Heavy Metals-4

- ◆ Advantages
 - Special iron powder with many holes on the surface, large specific area and physical and chemical absorption functions can remove Zn^{2+} , Cd^{2+} , Ni^{2+} which are considered difficult to treat theoretically.
 - Cr^{6+} is reduced to Cr^{3+} .
 - Fe-CN complex forms insoluble Fe-CN complex (Turnbull's blue) by the reaction with dissolved Fe^{2+} .
 - Accordingly simultaneous treatment of hazardous treatment is possible.
 - Rapid sinking velocity of the sludge, small sludge volume, good dehydration
 - Suitable for small sized wastewater treatment such as from laboratories containing kinds of heavy metals
- ◆ Disadvantages
 - A lot of sludge generation as a dry base.
 - Chelating agents should be treated by oxidation decomposition process in advance
 - Remained iron powder is hard to pump up or transportation.

10) Selective Chelate Ion-Exchange Method

- ◆ Chelate resin having the order in selectivity of heavy metals and having special functions to treat As^{3+} , BO_3^{2-} , F along with to treat normal heavy metals has been developed.
- ◆ Hg^{2+} is treated up to less than 0.0005 mg/L with chelate resin; however, the resin is impossible to regenerate.
- ◆ This method is also used for **recovery of the precious metals** such as Au^{3+} , Pt^{2+} , Pd^{2+} , Hg^{2+} , Ag^+ **and rare metals** such as Tl, In.

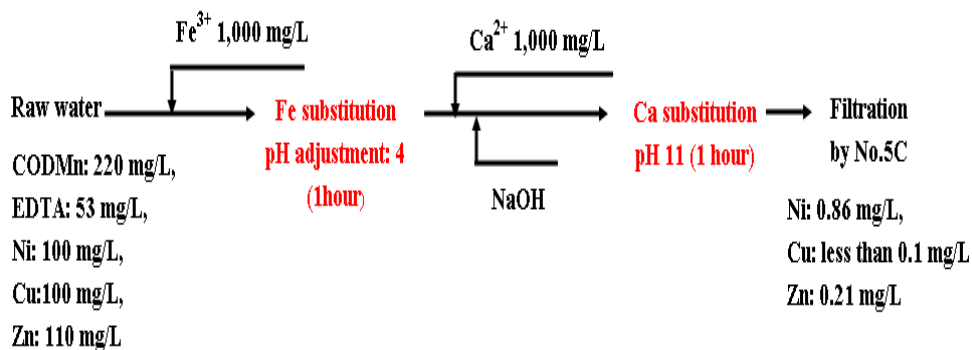
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Chelating Agents

Sorts	Cheleting agents	Nature
Oxycarbonic acid complex	Citric acid, tartaric acid, gluconic acid, etc	Forms complex with almost metals
Carbonic acid complex	Acetic acid, oxalic acid, malonic acid	Not stable as a complex. Form a precipitation of hydroxide by lime or calcium salt along with caustic soda
Amino-polycarbonic acid complex	EDTA (ethylenediaminetetraacetic acid), NTA (Nitrilotriacetic acid), etc	Forms stable complex with almost heavy metals. Nickel and chromium complex are extremely stable.
Ethanolamine complex	Mono, di, tri-ethanolamine, etc	Forms relatively stable complex with lead, copper, iron, etc.
Ammine complex	Ammonia, ethylenediamine, etc	Forms a stable complex at high concentration
Compounds with dispersion effects	Phosphate, carbonic salt, silicate, etc	Hinders precipitations of heavy metals

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Effects of Substitution treatment (Ni-EDTA complex)



Substitution method is applied at acid side due to an ion reaction as principal.

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Sludge Treatment

- 1) Solidification by cement or asphalt
- 2) Sintering with the mixture of other inorganic matters
 - ◆ **Melting process** where sludge is incinerated alone by its remained ash and the clinker is discharged
 - ◆ **Sintering process** where glass, clays, etc, are added to sludge as a sintering material. The sintering process is carried out at 800 to 1,000 °C.
 - ◆ Advantages
 - Reduction of waste volume, Stable
 - Sintered material is used for aggregate, bricks, etc.
 - ◆ Disadvantages
 - Limitation of sludge application due to volatilization of heavy metals
 - Re-dissolution of Cr to Cr⁶⁺
- 3) Chemical treatment by special sulfurous heavy metal fixing agent
- 4) Metal recycle
 - ◆ Segregation of sludge
 - Heavy metal, hydrogen fluoride acid or phosphoric acid
 - ◆ Sludge concentration by HDS method
 - ◆ Establishment of supply and transportation system

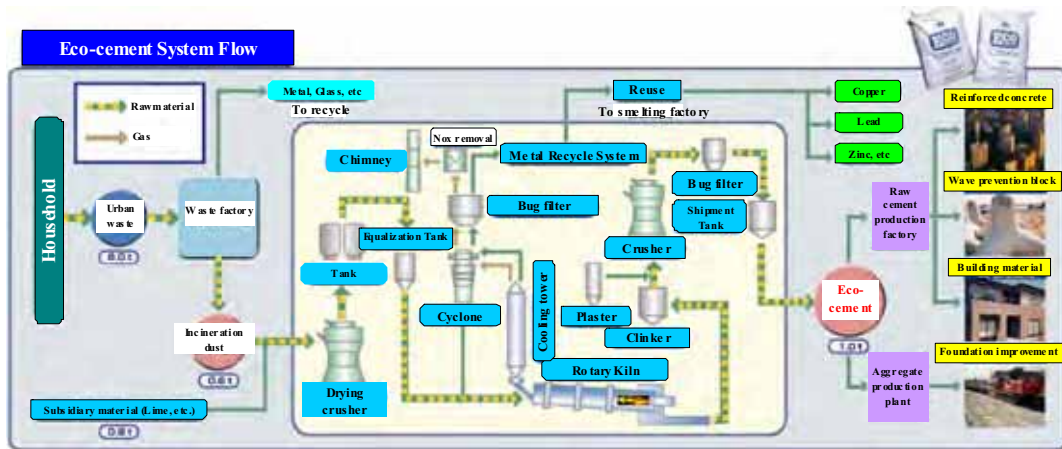
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Examples of metal recycles, etc. including in the stage of R & D.

- 1) Return to copper refinery of sludge from wastewater treatment of copper plating and copper foil
- 2) Recycle of nickel, chromium and iron from the sludge of stainless materials surface treatment
- 3) Electrode reduction recycle of plating waste liquid including precious metals such as gold, silver, palladium, etc.
- 4) By-product aluminum from the sludge of aluminum material surface treatment
- 5) Ferric ferrite production from acid cleaning and polishing of steel materials process
- 6) Recycle of zinc, cadmium, lead from the dust or residue generated in metal refinery processes
- 7) Recycle of hydrogen fluoride acid from calcium fluoride generated in semi-conductor production process
 - ◆ $\text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HF} + \text{CaSO}_4$

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Eco-Cement System Flow



Taiheiy Cement Corporation

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Waste Treatment by Kawasaki Eco-Town

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Treatment of Hazardous Substances-1

Hazardous Substances	Treatment method	Remarks	
Cadmium and lead	Hydroxide, substitution, sulfide methods		
Chromium (VI)	Reduction from to Cr^{3+}	<ul style="list-style-type: none"> ◆ By sulfurous acid salt <ul style="list-style-type: none"> - pH 2 to 2.5, ORP: 300 to 400 mV, changeable with the co-existence of other metals. - Excess addition of sulfurous acid salt brings about the dispersion of chromium (III). - A little excess addition of sulfurous acid salt brings about re-generation of chromium (VI). ◆ By ferrous sulfide <ul style="list-style-type: none"> - Wide range of pH - Waste liquid including ferrous sulfide can be used. - No chromium (VI) exists in effluent - Automatic control: pH 5 to 12, using DO meter ◆ Electrolysis reduction: Fe cathode <ul style="list-style-type: none"> - Acid addition due to pH increase during reaction - Suitable for concentrated liquid 	
		Ion exchange effluent	◆ Strongly basic anion-exchange resin to recover Cr^{6+} , Suitable for small sized treatment,
		Activated carbon	◆ pH 4-6; Saturated adsorption capacity; 10 to 20 mg- Cr^{6+} /g-AC; Effluent: 0.5 mg/L.

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Treatment of Hazardous Substances-2

Hazardous Substances	Treatment method	Remarks
Inorganic Mercury	Sulfide method including special sulfurous heavy metal fixing agent	
	Activated carbon	◆ Effective for inorganic and organic mercury, pH 1 to 6
	Mercury selective chelating resin	◆ Having sulfurous functional group
Organic Mercury	Oxidation by chlorine + sulfide method + (mercury chelate resin)	◆ Oxidation of organic mercury with small carbon number is more difficult to oxidize due to its stability.
Arsine	Co-precipitation	<ul style="list-style-type: none"> ◆ Change to As(V) by oxidation using chlorine, ozone, hydrogen peroxide ◆ As co-precipitation agent: Fe(III); Best pH: 4-5 ◆ Calcium + sodium carbonate is also effective to treat heavy metals simultaneously at pH over 10.5 ◆ Iron powder or ferrite method is also effective
		Chelate resin like selenium type chelate resin for As(III)
	Activated Alumina	

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Treatment of Hazardous Substances-3

Hazardous Substances	Treatment method	Remarks
Selenium	Co-precipitation by Fe (III)	<ul style="list-style-type: none"> ◆ Effective only for Se(IV); pH: below 6.2 ◆ Need experiment in advance
	Adsorption by activated alumina	<ul style="list-style-type: none"> ◆ Effective only for Se(IV) ◆ Saturated absorption amount: 0.24 mg-Se/L- activated alumina
	Ion exchange or R.O	<ul style="list-style-type: none"> ◆ Effective for Se (IV) and Se (VI)
	Reduction by metal iron	<ul style="list-style-type: none"> ◆ Wastewater containing acid Se(VI) with HCl passed through a column packed with metal ion at 50 °C, SV 15/hr. The reduction ratio is in proportion to Fe (II) dissolved. After then neutralization. ◆ Influenced by SO_4^{2-}; Pre-experiment is necessary ◆ Al, Cu, Zn are the candidates as reduction agents. ◆ Reduction by absorption agent prepared by Fe(III) and Pb. ◆ Study on Se (IV) and Se (VI) absorption of N-methyl-D-glucamine ion-exchange resin mainly being used for removing boron
	Biological reduction	<ul style="list-style-type: none"> ◆ Method using anaerobic bacteria which use Se for respiration to reduce to metal Se. In Japan a process where biological de-nitrification and removal of Se was developed by culturing selenium reduction bacteria; however, de-nitrification is prior to Se reduction. Accordingly, de-nitrification should be completed first, which brings about a big volume of de-nitrification tank.

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Treatment of Hazardous Substances-4

Hazardous Substances	Treatment method	Remarks
Boron	Coagulation-sedimentation process	<ul style="list-style-type: none"> ◆ pH over 9, Aluminum salt and calcium hydroxide by adsorption on $Ca(AlO_2)_2$ ◆ Treatment of fluoro boronic acid (HBF_4) needs other processes. ◆ One possibility is using ion-exchange to concentrate. Concentrated one is heat decomposition with calcium salt. ◆ Another is to use aluminum salt with heat to decompose HBF_4 to treat F.
	Adsorption (ion-exchange)	<ul style="list-style-type: none"> ◆ N-methyl-D-glucamine ion-exchange resin as OH type by NaOH, reclaim by sulfuric acid,
Fluorine	Calcium Fluoride method	<ul style="list-style-type: none"> ◆ By adding lime to fluorine forms insoluble calcium fluoride. The limit effluent quality is 10 to 20 mg-F/L; however, by HDS method, the quality becomes better, ◆ Suitable for 30 to 50 mg-F/L influent
	Hydroxyl co-precipitation method	<ul style="list-style-type: none"> ◆ F is absorbed on the surface of Aluminum hydroxide formed by aluminum salt at pH 6 to 7 ◆ Effluent less than 8 mg-F/L ◆ Suitable for influence with less than 20 to 30 mg-F/L ◆ Similar process is using magnesium hydroxide, pH 10 to 11, this method will remove heavy metal hydroxide simultaneously
	Adsorption	<ul style="list-style-type: none"> ◆ by selective ion exchange resin

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Treatment of Hazardous Substances-5

Hazardous Substances	Treatment method	Remarks
Cyanogens	Alkali Chlorination	<ul style="list-style-type: none"> ◆ First stage: pH more over 10, ORP 300 – 350 mV ◆ Second stage: pH 7 -8, ORP: 600 -650 mV ◆ $Cl_2/CN \approx 7$ ◆ Applicable for NaCN, KCN, Cu-CN complex, Zn-CN complex and Cd-CN complex ◆ Decomposition of Ni-CN and Ag-CN needs excess chlorine and long retention time. ORP control is not suitable but constant feed is used at normal temperature. Under the temperature 40 -50 °C, Ni-CN complex is easily decomposed in accordance with theory and ORP control is applicable. ◆ Fe-CN, Co-CN, Au-CN complexes are stable, not being decomposed even by excess chlorine. Accordingly, these complexes are treated by absorption or insoluble salt formation process.
	Oxidation by ozone	<ul style="list-style-type: none"> ◆ pH more over 9.5 ◆ Trace of Cu or Mn acts as a positive catalyst ◆ Decomposition of Ni-CN is possible. ◆ Decomposition of Fe-CN, Co-CN, Au-CN is not possible
	Electrode oxidation	<ul style="list-style-type: none"> ◆ Suitable for concentrated liquid waste ◆ Not suitable for Fe-CN or Ni-CN complex.

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Treatment of Hazardous Substances-6

Hazardous Substances	Treatment method	Remarks
Cyanogens	Turnbull's blue to formulate $(Fe_3[Fe(CN)_6]_2)$	<ul style="list-style-type: none"> ◆ Suitable for Fe-CN ◆ Lack of Fe to be added produces soluble $Fe [Fe(CN)_6]^-$ ◆ Suitable pH is 5-6 because high pH causes soluble Fe-CN complex. ◆ Applicable after alkali chlorination ◆ ORP control or DO monitoring and control because ferrous salt reacts Turnbull's blue \rightarrow residual chlorine \rightarrow DO. To measure DO decrease
	Formation of insoluble CN-complex	<ul style="list-style-type: none"> ◆ Cu, Mn, Zn in place of Fe can form insoluble Fe-CN complex. pH :8 in this method. ◆ Suitable for kinds of CN-metal complexes and free CN. ◆ Used for recovery of precious metals from Au-CN, Ag-CN
	Biological Treatment	<ul style="list-style-type: none"> ◆ By activated sludge process after bacteria culture ◆ As an example, Influent 20 -50 mg-CN/L, 0.4 – 0.8 kg/CODMn/m³/day, removal rate of CN: more than 98 %
	Absorption	<ul style="list-style-type: none"> ◆ By ion-exchange resin or by activated carbon. Generally this method is used only as non-regeneration. ◆ Recovery of Au. After saturation, the absorption materials are incinerated to recovery of Au.
	Acid decomposition-incineration	<ul style="list-style-type: none"> ◆ pH less than 1 CN complex is decomposed and produces CN gas, CN gas is trapped by NaOH to form NaCN or incinerated (more than 900 °C) to CO₂ and N₂ gas

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Treatment of Hazardous Substances-7

Hazardous Substances	Treatment method	Remarks
Cyanogens	Evaporation-melting process	<ul style="list-style-type: none"> ◆ CN compounds are decomposed at high temperature. Evaporated residue is decomposed at 1,200 °C to CO₂ and N₂ and metal residue is recovered. The liquid separated at evaporation process contains NH₃ and part of CN to be treated. ◆ Suitable for concentrated CN compounds. ◆ This method needs boiler for concentration, cooling tower, blast Furnas, exhausted gas treatment, alkali decomposition apparatus for liquid separated at evaporation, etc. ◆ Costly
	Wet heating hydrolysis decomposition process	<ul style="list-style-type: none"> ◆ This method is heating (more than 150 °C by 1.1 MPa boiler) CN compounds at pressurized vessel to form NH₃ and formic acid salt by NaOH. ◆ When CN is completely decomposed, metals formed CN complex to change metal oxide.
Nitrogen (NH ₄ -N, NO ₂ -N, NO ₃ -N)	Biological treatment	<ul style="list-style-type: none"> ◆ Biological nitrification-denitrification
	Ammonia stripping	<ul style="list-style-type: none"> ◆ Target: NH₄-N, High pH by NaOH, eliminate as NH₃ gas by aeration or scrubber, high performance with high temperature, eliminated NH₃ is recovered as ammonium sulfate
	Break-point chlorination	<ul style="list-style-type: none"> ◆ Target: NH₄-N, decomposing of NH₄-N to N₂ gas by chlorine. Suitable for low concentration of NH₄-N, ORP control. Possibility of generation of tri-halomethane, a carcinogen.

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Treatment of Hazardous Substances-8

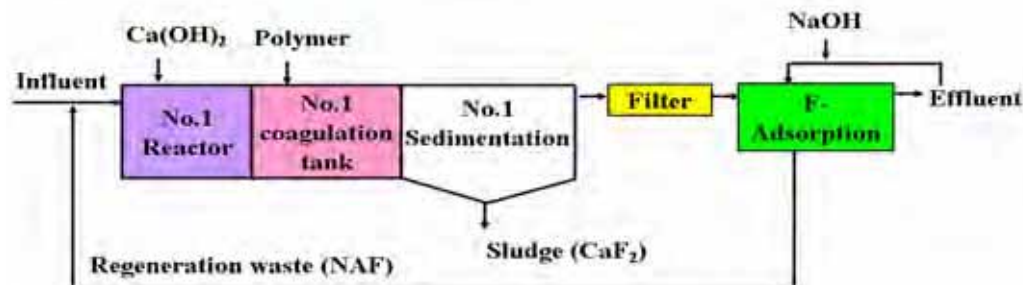
Hazardous Substances	Treatment method	Remarks
Nitrogen (NH ₄ -N, NO ₂ -N, NO ₃ -N)	Ion-exchange	<ul style="list-style-type: none"> ◆ Zeolite or cation ion exchange resin for NH₄ ion, Anion ion exchange resin for NO₂, NO₃ ion. Treatment of reclaimed liquid containing concentrated nitrogen is necessary. Zeolite or ion-exchange resins are low in selectivity.
	Decomposition with catalyst	<ul style="list-style-type: none"> ◆ Decomposition of NH₄-N to N₂ gas at high temperature and high pressure with the help of oxygen and catalyst (precious metal or metal oxide). Suitable for high concentrated NH₄-N liquid like regeneration liquid of ion-exchange treatment
Organophosphorus Pesticides (Parathion, Methyl Parathion, EPN (O-ethyl O-4-nitrophenyl phenylphosphonot hioate), Methyl Dimethone: insecticide	Biological treatment	<ul style="list-style-type: none"> ◆ Hydrolysis at high pH → coagulation-sedimentation → filtration → dilution → activated sludge
	Activated carbon	<ul style="list-style-type: none"> ◆ Main target: parathion
Organic pesticide (1,3-dichloropropene (D-D), Thiuram, Simazine (CAT), Thiobencarb): disinfectant and weed killer	Activated carbon	<ul style="list-style-type: none"> ◆ Absorption capacity is small
	RO	<ul style="list-style-type: none"> ◆ Treatment of concentrated liquid and cleaning wastewater is still an issue

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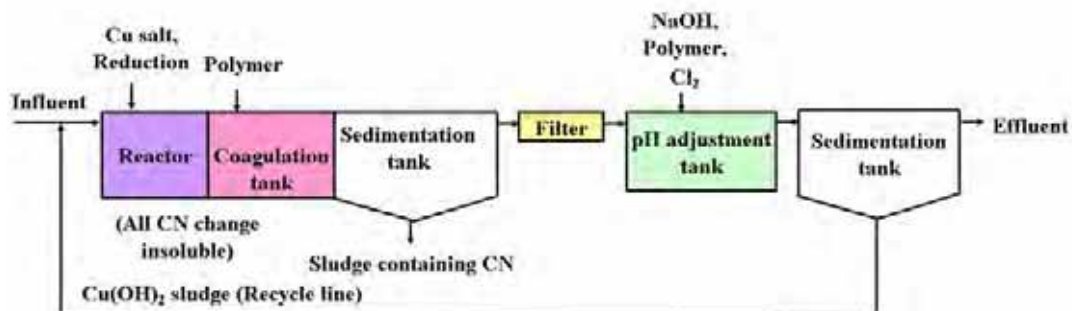
Treatment of Hazardous Substances-9

Hazardous Substances	Treatment method	Remarks
PCB (polychlorobiphenyl)	Coagulation-sedimentation-slow filtration or MF	◆ Coagulation-absorption by using kaolin and aluminum sulfate
	Activated carbon	◆ Target: chlorine number 1-3, need pre-experiment
	Base Catalyzed Decomposition(BCD)	◆ De-chlorination of PCB by heating at 300 to 350 °C with N ₂ gas with the helps of oil with high boiling point, carbon catalyst and KOH.
	Supercritical Water Oxidation (SCWO)	◆ Decomposition by supercritical water oxidation ((400 °C, 25MPa)
	Bioremediation using white rot fungus	◆ Treatment of dioxin-contaminated soil White rot fungus is a common fungus that causes wood decay; it excretes lignin-degrading enzymes with highly active oxidizing properties that can decompose various organic compounds.
Volatile Organic Compounds	Aeration	◆ By stripping tower, for Trichloroethylene 190 – 230 g/day 20 m ³ -air/m ³ -wastewater/hr, for Tetrachloroethylene 39 – 183 g/day 120 m ³ -air/m ³ -wastewater/hr, eliminated gas is treated by absorption or oxidation decomposition
	Activated carbon adsorption	◆ Absorption capacity is very small, pre-experiment is necessary
	Oxidation decomposition	◆ By KMnO ₄ at high temperature, H ₂ O ₂ +UV with TiO ₂ catalyst
	Biological treatment	◆ By special bacteria in the soil to decompose Volatile Organic Compounds, activated sludge

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F removal by combination of F-absorption Resin



CN removal by Formulation of Insoluble Salt by Cu-salt

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Analysis of Hazardous Substances-1

Parameter	Analysis method	Remarks
Chromium (VI) (Cr⁶⁺)	Diphenylcarbazide absorptiometry	<ul style="list-style-type: none"> ◆ Use the reference solution where a little amount of ethanol to change chromium (VI) to chromium (III) ◆ Reduction substances give negative influence. In this case, use Fe co-precipitation to separate chromium (VI)
	Flame atomic absorption method	<ul style="list-style-type: none"> ◆ Filtrate by Fe co-precipitation
	Electric heating atomic absorption method	
	ICP atomic emission spectrometry	
	ICP mass spectrometry	
Arsenic (As)	Diethyldithiocarbamic acid silver salt absorptiometry	<ul style="list-style-type: none"> ◆ Change As (V) to As(III) with KI and SnCl₂. ◆ Generated H₂S is fixed by lead acetate solution ◆ Keep 25 °C in a water bath
	Atomic absorption method by hydride	<ul style="list-style-type: none"> ◆ Change As(III) to arsenic hydride by Zn powder ◆ Use hydrogen- argon flame ◆ When a lot of organic matter is contained, decompose the organic matter with H₂SO₄, HNO₃, HCl₄ ◆ Use the beaker made of ethylene tetra fluoride resin

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Analysis of Hazardous Substances-2

Parameter	Analysis method	Remarks
Arsenic (As)	Atomic absorption method by hydride	<ul style="list-style-type: none"> ◆ Contamination of Zn powder to generate hydride, Sodium tetrahydroborate is preferable to use instead of Zn. ◆ Instead of hydrogen-argon flame, a heating-type absorption cell is serviceable.
	ICP atomic emission spectrometry by hydride	<ul style="list-style-type: none"> ◆ Change As (V) to As(III) with HCl and KBr in order to reduce selenium (Se) simultaneously . ◆ Change As(III) to arsenic hydride by NaBH₄ and HCl ◆ Use standard addition method for calibration curve and background correction
Total mercury (Notice 59, Ministry of Environment, 1971)	Atomic absorption spectrometry by reduction and vaporization	<ul style="list-style-type: none"> ◆ Pretreated sample using KMnO₄, and reduce Hg II by SnCl₂. Aerate this solution to generate mercury vapor, and measure its atomic absorption. ◆ Be careful of lots of chloride ion. Reduction by excess hydroxyl ammonium solution. ◆ Benzene or acetone gives positive error. When complicated substances exist, extract mercury as dithizone complex, measure owing to heating and vaporation method.
	Atomic absorption spectrometry by heating and vaporization	<ul style="list-style-type: none"> ◆ Pretreated sample using KMnO₄, and extract dithizone complex of mercury with organic solvent from the solution acidified by H₂SO₄. After volatilizing organic solvent, heat residue to emit mercury vapor, measure its atomic absorption.

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Analysis of Hazardous Substances-3

Parameter	Analysis method	Remarks
Alkyl mercury(II) compound (Notice 59, Ministry of Environment, 1971)	Gas chromatography	<ul style="list-style-type: none"> ◆ Extract alkyl mercury(II) compound in benzene, back-extract selectively it using L-cysteine, extract again using benzene, and measure by the gas chromatography with ECD detector. ◆ When the sample contains sulfide ion or thiocyanate ion, remove it by powdered CuCl_2. ◆ In case of existing a lot of inorganic mercury, repeat washings until a washing shows neutrality because residual HCl in benzene layer causes incomplete back-extract of alkyl mercury owing to L-cysteine. ◆ When the sample contains the constituent interfering benzene extraction of alkyl mercury(II) compound, add definite amount of ethyl mercury chloride or methyl mercury chloride reference solution, find the recovery rate and correct the determined value.
	Thin layer chromatograph separation-atomic absorption spectrometry	<ul style="list-style-type: none"> ◆ Extract alkyl mercury(II) compound in benzene, and concentrate it in alumina column. Separate it with thin-layer chromatography, peel off the spots corresponding to alkyl mercury and measure it by atomic absorption spectrometry in accordance with the reduction procedures for total mercury. ◆ When phenyl mercury exists in sample, use 1- butanol saturated with water as developing solvent.

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Analysis of Hazardous Substances-4

Parameter	Analysis method	Remarks
Selenium (Se)	3,3'-diaminobenzidine absorptiometry	<ul style="list-style-type: none"> ◆ Concentrate selenium by co-precipitation with $\text{Fe}(\text{OH})_3$, and 3-3'-diaminobenzidine to form selenium complex. ◆ Adjust pH by using pH meter.
	Atomic absorption method by hydride	◆ Same as analysis of As
	ICP atomic emission spectrometry by hydride	
Boron (B)	Methylene blue absorptiometry	<ul style="list-style-type: none"> ◆ Add H_2SO_4 and HF to fluoride compound to make tetrafluoroborate ion, add methylene blue, extract produced ion association by 1,2-dichloroethane, and measure its absorbance. ◆ Use Na_2CO_3 to melt organic matter when a lot of organic matter co-exists. ◆ Chromate ion makes disturbance. To prevent this disturbance; add H_2O_2 and boil it to decompose excessive H_2O_2. ◆ Use water prepared using a still made of quartz glass or metal ◆ Use glassware made of quartz or soda lime glass ◆ Use separatory funnel made of polyethylene

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Analysis of Hazardous Substances-5

Parameter	Analysis method	Remarks
Boron (B)	Azomethine H absorptiometry	<ul style="list-style-type: none"> ◆ React with azomethine H under pH about 6 to generate yellow complex. ◆ The existence of Fe, Mn, Al, Cu, Be, Ti, V, Zr gives positive error.
	ICP atomic emission spectrometry	<ul style="list-style-type: none"> ◆ For the sample containing high concentration of salts, the standard addition method is used along with correction of background ◆ Before spraying other solution, long time of spraying water is necessary to eliminate the longer memory effect.
	ICP mass spectrometry	<ul style="list-style-type: none"> ◆ Use internal standard method by using yttrium (Y) or indium (In) ◆ When sample contains high concentration of salt, dilute with water to a certain concentration ◆ Before spraying other solution, long time of spraying water is necessary to eliminate the longer memory effect.
Fluorine compound (F)	Lanthanum-alizarin complexone absorptiometry	<ul style="list-style-type: none"> ◆ Pre-treat the sample by distillation (temperature $145 \pm 5^\circ\text{C}$), distilling rate 3 to 5 ml/min. ◆ Add several drops of NaOH solution in receiver when a lot of halogenide other than fluoride ion is contained in the sample. ◆ Keep pH 4.3-4.6 in the reaction.

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Analysis of Hazardous Substances-6

Parameter	Analysis method	Remarks
Fluorine compound (F)	Ion-selective electrode method	<ul style="list-style-type: none"> ◆ Pre-treat the sample by distillation (temperature $145 \pm 5^\circ\text{C}$), distilling rate 3 to 5 ml/min. ◆ pH, liquid temperature, co-existence substances, response time, characteristics of electrode, etc.influence the result. ◆ Keep the electrode clean ◆ Potential discrepancy between fluoride ion reference solution (1mg-F/l) and fluoride ion reference solution (100 mg-F/l) falls in the range of 100 -125 mV (25°C), and the working curve makes linearity between 0.1 mg-F/l and 100 mg-F/l concentration of fluoride ion.
	Ion chromatography	<ul style="list-style-type: none"> ◆ Detector: Electric conductivity detector ◆ Pre-treat the sample by distillation (temperature $145 \pm 5^\circ\text{C}$), distilling rate 3 to 5 ml/min. ◆ Check periodically the performance of a separation column.
Total cyanide (CN)	Pyridine-pyrazolone absorptiometry	<ul style="list-style-type: none"> ◆ Pre-treat the sample by distillation (pH below 2), distilling rate 2 to 3 ml/min. ◆ The pH for coloring should be in the range from 6 to 8. ◆ The color becomes the strongest within 30 minutes after color reaction and the color keeps one hour at 25°C.

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Analysis of Hazardous Substances-7

Parameter	Analysis method	Remarks
Total cyanide (CN)	4-pyridinecarboxylic acid-pyrazolone absorptiometry	<ul style="list-style-type: none"> ◆ Pre-treat the sample by distillation (pH below 2), distilling rate 2 to 3 ml/min. ◆ The color becomes the strongest within 20 minutes after color reaction and the color keeps one hour at 25 °C. ◆ The pH for coloring should be in the range from 7 to 8.
	Ion-selective electrode method	<ul style="list-style-type: none"> ◆ Measure the pre-treated sample at pH 12 to 13
Ammonium ion (NH ⁴⁺)	Indophenol blue absorptiometry	<ul style="list-style-type: none"> ◆ Pre-treat the sample by distillation, distilling rate 5 to 7 ml/min. ◆ Liquid temperature between 20 to 25 °C gives the maximum coloring after nearly 30 mins, and it is stable for another about 30 mins.
	Neutralization titrimetry	<ul style="list-style-type: none"> ◆ Pre-treat the sample by distillation, distilling rate 5 to 7 ml/min. ◆ Amines in the sample move to receiver and give positive error. In this case, use indophenol blue absorptiometry.
	Ion-selective electrode method	<ul style="list-style-type: none"> ◆ Control the pH of pretreated sample to 11 to 13 so as to convert ammonia ion into ammonia.
	Ion chromatography	<ul style="list-style-type: none"> ◆ Detector: Electric conductivity detector ◆ The sample containing organic matter (proteins, oils and fats, surface-active agents, etc.) shall be filtered through UF to remove them as completely as possible, and then be tested.

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Analysis of Hazardous Substances-8

Parameter	Analysis method	Remarks
Ammonium ion (NH ⁴⁺)	Ion chromatography	<ul style="list-style-type: none"> ◆ When sample contains cations such as calcium or magnesium, prepare the eluent 20 times to 200 times concentrated than that of eluent periodically, and pour ◆ For the sample containing oxidizing material or reducing material, dilute the sample with water by a definite rate.
Nitrite ion (NO ₂ ⁻)	Naphthylethylenediamine absorptiometry	<ul style="list-style-type: none"> ◆ Filtrate sample through filter paper 5 grade C or filter paper 6 grade. When filtration can not remove coloring or turbidity, use coagulation- filtration.
	Ion chromatography	<ul style="list-style-type: none"> ◆ When anions other than nitrite ion are simultaneously tested, use anion mixed reference solution as designated.
Nitrate ion (NO ₃ ⁻)	Indophenol blue absorptiometry after reducing distillation	<ul style="list-style-type: none"> ◆ Remove ammonia by distillation with addition of NaOH in sample, and add Devard's alloy to reduce nitrite ion and nitrate ion into ammonia, distill it to receiver, ◆ Liquid temperature between 20 to 25 °C gives the maximum coloring after nearly 30 mins, and it is stable for another about 30 mins.
	Neutralization titrimetry after reducing distillation	<ul style="list-style-type: none"> ◆ Remove ammonia by distillation with addition of NaOH in sample, and add Devard's alloy to reduce nitrite ion and nitrate ion into ammonia, distill it to receiver,
	Naphthylethylenediamine absorptiometry after copper-cadmium column reducing	<ul style="list-style-type: none"> ◆ Reduce nitrate ion in sample by copper-cadmium column to make it nitrite ion ◆ Filtrate sample through filter paper 5 grade C or filter paper 6 grade. When filtration can not remove coloring or turbidity, use coagulation- filtration.

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Analysis of Hazardous Substances-9

Parameter	Analysis method	Remarks
Nitrate ion (NO ₃)	Naphthylethylenediamine absorptiometry after copper-cadmium column reducing	<ul style="list-style-type: none"> Liquid flowing out contains about 50 mg-Cd/L includes. Treat it appropriately.
	Brucine absorptiometry	<ul style="list-style-type: none"> In case of strong alkalinity, test it after controlling its pH around 7 The coexistence of such Fe (II), Fe (III), or manganese (II) results in positive error, but 1mg/l or less of their concentration will give no problem. The reaction between nitrate ion and brucine gets faster in proportion as temperature rises higher. Therefore, operate at the same temperature as that at calibration curve preparation.
	Ion chromatography	<ul style="list-style-type: none"> When anions other than nitrate ion are simultaneously tested, use anion mixed reference solution as designated.
Organophosphorus (EPN, parathion, methyl parathion)	Gas chromatography(Notice 64, Ministry of Environment)	<ul style="list-style-type: none"> Extract organophosphorus by hexane and concentrate using evaporator or Kuderna Danish apparatus and inject the concentrated in GC (FPD type) In case disturbance peak appears by impurities, separate the impurities by using SiO₂-diatomite column, florisil column or thin-layer chromatography.
	Naphthylethylenediamine absorptiometry (Averell-Norris method)	<ul style="list-style-type: none"> Pretreat the sample by extracting with hexane with, separate by using SiO₂-diatomite column, and remove the disturbances

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Analysis of Hazardous Substances-10

Parameter	Analysis method	Remarks
Organophosphorus (EPN, parathion, methyl parathion)	Naphthylethylenediamine absorptiometry (Averell-Norris method)	<ul style="list-style-type: none"> Reduce organic phosphorus pesticides, diazotize it using nitrous acid, decompose excess nitrous acid using ammonium amidosulfate, couple it with N-1-naphthylethylenediamine.
	p-nitro phenol absorptiometry	<ul style="list-style-type: none"> Pretreat the sample by extracting with hexane with, separate by using SiO₂-diatomite column, and remove the disturbances Hydrolyze organic phosphorus pesticide with alkali, produce yellow p-nitrophenoxide, and measure its absorbance.
Methyldimethone	Molybdenum blue (tin chloride reductional absorptiometry) (Notice 64, Ministry of Environment, 1974)	<ul style="list-style-type: none"> Pretreat the sample using thin layer chromatography with CHCl₃, dissolve it to PO₄³⁻, and color with ammonium molybdate with tin chloride.
Thiuram	High Performance Liquid Chromatography (Notice 59, Ministry of Environment, 1971)	<ul style="list-style-type: none"> Extract sample by dichloromethane as acetonitrile solution or using solid phase of co-polymer of styrene and divinylbenzene to absorb thiuram and flow out it by acetonitrile. And inject it to HCLP (High Performance Liquid Chromatography).
Simazine and Thiobencarb	Gas chromatography (Notice 59, Ministry of Environment, 1971)	<ul style="list-style-type: none"> Extract sample by dichloromethane and concentrate by hexane or using solid phase of co-polymer of styrene and divinylbenzene to absorb simazine and thiobencarb and flow out it by hexane. And inject it to Gas chromatography (NPD or ECD type)

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Analysis of Hazardous Substances-11

Parameter	Analysis method	Remarks
Simazine and Thiobencarb	Gas chromatography-Mass spectrometry (Notice 59, Ministry of Environment,1971)	◆ Inject the hexane concentrated extract in GC with split less injection method or cold-on column injection method and monitor mass numbers peculiar to simazine and thiobencarb using selective ion monitor
Polychlorinated biphenyl (PCB)	Gas chromatography (Notice 59, Ministry of Environment,1971)	◆ Extract PCB by hexane, hydrolyze with alkali agent, concentrate it by hexane again. Flow the concentrated PCB in silikagel column, collect effluent equivalent for the effluent fraction confirmed by PCB standard in advance. Concentrate the effluent by hexane and inject it in Gas chromatography (ECD detector)
	Gas chromatography-Mass spectrometry	◆ Add NaCl and internal standard to sample, extract PCB and internal standard by hexane to concentrate. Flow the concentrated them in silikagel column, concentrate separated effluent again. Add perylene-d ₁₂ . Inject a certain amount of it to GC-MS using selective ion monitor or total ion monitor.
Volatile Organic Compounds	Purge trap method or head space method -Gas chromatography Mass Spectrometry	◆ (Purge and trap method) Add internal standard fluorobenzene to sample. Collect volatile organic compounds in trap tube. Heat the trap tube to de-absorb them and cool to absorb them on cooling condensation apparatus. Heat again and inject the concentrated sample to GC-MS using selective ion monitor.

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Analysis of Hazardous Substances-12

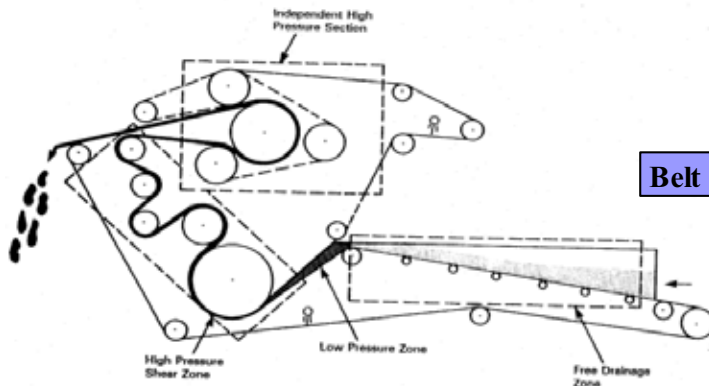
Parameter	Analysis method	Remarks
Volatile Organic Compounds	Purge trap method or head space method -Gas chromatography	◆ (Purge and trap method) Add internal standard (fluorobenzene) to sample. Collect volatile organic compounds in trap tube. Heat the trap tube to de-absorb them and cool to absorb them on cooling condensation apparatus. Heat again and inject the concentrated sample to GC-MS using selective ion monitor.
	Solvent extraction-Gas Chromatography	◆ For Tetrachloromethane, Tetrachloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, Trichloroethylene (TEC). Extract them in sample by hexane and inject concentrated sample in Gas ◆ More than 20 mg/l of mineral oil disturbs the result.

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Characteristics of Dehydrator

	Belt Filter	Centrifuge	Filter Press
Capacity	90 to 130 kg-solid waste/m ² /hour	~50 m ³ /hour	2 to 4 kg-sludge solid/m ² /hour
Moisture contents (%)	76 to 80 % with the addition of polymer of 1 % to dried sludge.	78 to 82 % with the addition of polymer of 1 % to dried sludge.	63 to 65 % with the addition of lime and ferrous of 30 to 40 % and 5 to 10 %, respectively, to dried solid
Continuous operation	Yes	Yes	NO
Maintenance	Relatively easy due to simple structure	Relatively easy.	Relatively difficult
Incidental facilities	-	Less	Many
Installation area	A little bit bigger than other types of dehydrator	Small	Large
Electricity consumption	Relatively small	Relatively big	Relatively big and running cost is high
Others	Splintery facilities are relatively fewer Zigzag of filter cloth to be paid attention.	Counter measures to vibration and removal of sand and impurities	One process of filtration-sludge discharge-filter media washing: 20 to 40 mins.

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Belt press Filter



Centrifuge (Tanabe)



Filter Press

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Oxidation Ditch Process



Natural Pond Process

*Thank you for your attention.
See you again.
IZAWA Tetsuo*