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PROJECT IN THE REPUBLIC OF KOREA
REPORT ON MISSION

DP/ROK/82/030/A/11-53/31.8.F

BY

Republic of Korea.

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AND WASTE WATER TREATMENT

AT
KIMM KOREA INSTITUTE OF MACHINERY AND METALS
CHANG-WON, KYONGSANG-NAMDO, ROK

4007

from 15 April to 14 May 1985

ACKNOWLEDGMENT

I am grateful to Dr. Kwon, head of the Surface Treatment Laboratory at KIMM, and all his staff for their co-operation, kindness and friendly support during my work with KIMM and my stay in Chang-Won. Especially to my counterpart, Mr. Ro Byong-Ho, I owe a heartful 'thank-you'; he organised my programme and visits, was very helpful in many private cases and showed great endurance and acceptance of the deluge of device and information passed on to him during the mission.

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I. EXPLANATORY NOTES

The value of the Korean currency at the time of this mission was 865 Won per US$.

Units of measure used in this report and not SI-sanctioned are

h	for hour
d	for day
w	for week
m	for month
a	for year

$$\text{val} = \frac{\text{atomic or ion-weight}}{\text{valency}}$$

$$1 \text{ val} = 1000 \text{ mval}$$

All other units used correspond to the SI-regulations.

II. ABSTRACT

Under the title 'Expert in Waste Water Treatment', Project-No. DP/ROK/82/030/A/11-53/31.8.F, assistance was provided in the treatment of waste water from the surface finishing industry to the Surface Treatment Centre of KIMM Korea Institute of Machinery and Metals, Chang-Won/Masan, ROK. The special requirements of this mission were to review the Centre's programme and capability in waste water treatment, to suggest a research programme and to train the Centre's staff accordingly, to support the Centre in establishing contacts to institutes and organizations abroad and to present papers to the Centre's staff and industrial environment control engineers. The duration was one month.

In the Surface Treatment Centre up to know there existed no special waste water treatment programme and corresponding equipment and facilities; however, very good staff capability was found. The Pollution Control Group of KIMM has great experience in the general waste water field and strong influence on the development of waste water handling and technique in Korea, but not the necessary extensive knowledge of surface finishing. KIMM's Chemical Analysis Laboratory covers excellently the requirements of waste water analysing.

During the mission a basic introduction and staff training was provided; it was concentrated on the development of a waste water treatment scheme and plant design of the Bu-Chan industrial complex near Seoul consisting of seven plating shops. This training represented the main activity of the mission and provided a detailed knowledge of working method, calculation formula, various treatment techniques, chemical reactions and flow-rinsing circuit via ion-exchangers. In addition two field visits were paid and two papers prepared and presented.

The main result of this mission is the recommendation to build up the Waste Water Section within the Surface Treatment Centre without delay, to set up a work programme and to gain further knowledge and practical experience by intensive and organized education, field visits, collecting industrial problems and finally starting research work and support to industry in one to two years time.

III. INTRODUCTION

In order to support and sustain further industrial growth and to promote measures to increase the marketability of Korean surface-treated products a Surface Treatment Centre was established at KIMM Korean Institute of Machinery and Metals in Chang-Win within the frame of a four years' Government Project supported by UNIDO. One major function of the Surface Treatment Centre is to deal with the problems of waste water treatment and discharge by research work, assisting individual industries by solving specific problems, acting as an information centre and cooperating with institutes and manufacturing industries associated with waste water treatment technologies.

The purpose of the mission which produced this report was

- to review the Centre's programme an capability in waste water treatment,
- to suggest a research programme and to train the Centre's staff in the field of waste water treatment and discharge,
- to support the Centre in establishing contacts to institutes and organizations abroad,
- to present seminars to the Centre's staff and industrial environment control engineers.

The mission started at 15 April 1985 and ended at 14 May 1985. Although its total duration was one month (i. e. 26 working days) after reduction of breifing and debriefing as well as travelling time only three weeks were available for the actual work. The time for preparing this report (four days) was spent extra to the one month duration. In detail the time distribution on the various subactivities was as follows:

Introduction into KIMM	1	day	3,8 %
Programme and cabability review	2	days	7,7 %
Staff training	8	days	30,7 %
Field visits incl. report	1,5	days	5,8 %
Seminar preparation and presentation	4	days	15,4 %
Contact establishing	0,5	days	1,9 %
Total subactivities	17	days	65,3 %

(to be cont'd)

Total subactivities	17	days	65,3 %
Briefing, debriefing, travelling	9	days	34,7 %
Total working time	26	days	100,0 %

RECOMMENDATION: In the case of further missions it should be carefully considered whether it is efficient to restrict their duration just to one month; the minimum duration should be six weeks up to two months.

The original objectives of the mission could be attained except in the cases of staff training and research programme suggestion. Until this activity the Centre's staff did not have any knowledge and practical experience in waste water treatment and discharge, so that the main activity had to deal with a basic and fundamental staff training. Further theoretical and praxis training is necessary before the basis for efficient and successful research work will be available.

In accordance to Dr. Kwon's special conception the staff training itself was concentrated on the development of a conceptual design of a waste water treatment scheme and plant of an industrial complex of seven plating shops. This type of training could provide a maximum of practical working experience and theoretical background information within the given time.

IV. REVIEW OF WORK PROGRAMME, FACILITIES, EQUIPMENT AND STAFF CAPABILITY

A. Work programme

In the field of waste water treatment the major functions of the Surface Treatment Centre are basically fixed to

- deal with problems by research,
- assist industry by solving problems,
- act as an information centre,
- cooperate with institutes and manufacturing industries;

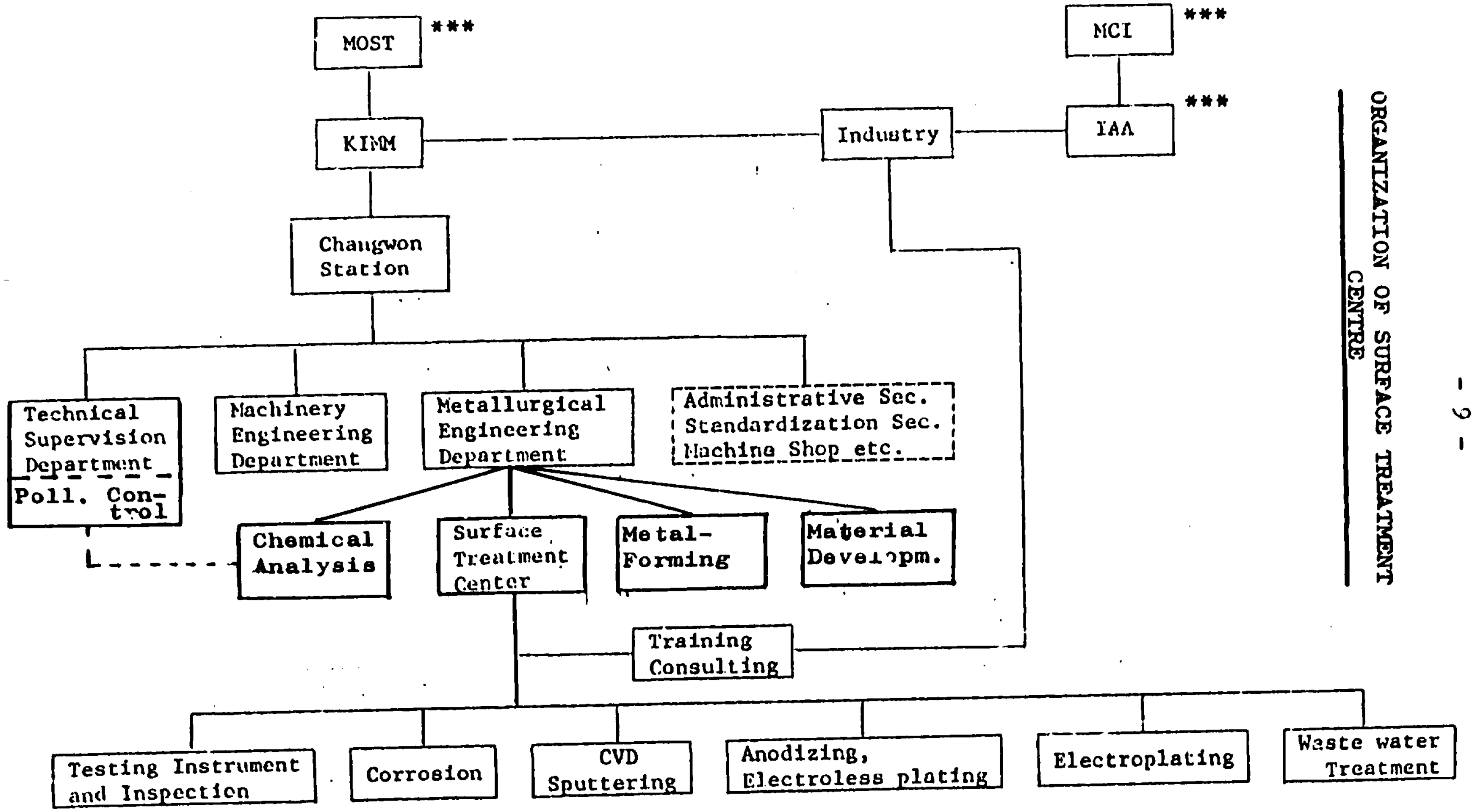
but there is no detailed programme how to realize these intentions.

B. Facilities and equipment

Next page 9 shows the organization which the Surface Treatment Centre is imbedded in; the graph was taken from the Government Project Document (Title: Surface Treatment Centre) and supplemented during this mission.

Within the Technical Supervision Department there is a section "Pollution Control", which Mr. Kwon Young-Bae (not Dr. Kwon Sik-Chol, head of the Surface Treatment Centre!) is in charge of. He is supported by Mr. Kim. Their field of activity is air- and water-pollution control, and so to some extent they also deal with waste water in the surface treatment industry. In addition Mr. Kwon is a member of the "Suggestion and Control Committee of the Korea Environment Office", which works independantly on any ministry and amongst others controls every environment protection investment and installation in Korea; it decides whether or whether not the investmen and installation proposed will be realized. Furthermore Mr. Kim is in charge of the waste water treatment plant going to be installed with KIMM. So in the Pollution Control Group there exists a great experience in the general waste water field combined with strong influence on the present and future development of waste water handling in Korea. However, a necessary knowledge about surface treatment and a specialization on the treatment of waste water from the surface treatment industry is not available.

ORGANIZATION OF SURFACE TREATMENT CENTRE



*** MOST: Ministry of Science and Technology
MCI : Ministry of Commerce and Industry
IAA : Industrial Advancement Administration

Mr. Kwon is also head of the Chemical Analysis Laboratory, which Mr. Kim also belongs to. There already waste water analysises in accordance to Korean standards are carried out. The laboratory is very well equipped (amongst others with Atomadsorption-Spectografy, Spectrofotometer, BOD-Incubator, COD-Analyzer, Oil-Content-Analyzer); it would be worth to purchase in addition just equipment for COD-single-probe-analysis, a portable laboratory-fotometer as well as handtest-sets for quick waste water analysis both in the laboratory and in the industry and finally an Imhoff-Cone for sludge-determination. As a result of this situation it can be said that the analytical side of waste water treatment and control is excellently covered by the Chemical Analysis Laboratory.

The Surface Treatment Centre itself does not yet have any facility and equipment for handling waste water problems and carrying out corresponding research work.

On the engineering side generally there are no facilities and equipment with KIMM except the new waste water treatment plant which possibly also could be used for pilot plant and testing work.

C. Staff capability

The staff of the Surface Treatment Centre consists of Dr. Kwon, nine graduated people and two technicians. Dr. Joe Edwards report (DP/ROK/82/030/A/11-52/31.8.F) describes in detail the capability of seven graduates; since that time two further fellows joined the Centre:

- Mr. Baek Un-Sung. He obtained the M. Sc. degree in material sciences and is in charge of Chemical Vapour Deposition.
- Mr. Lee Keon-Hwan. He obtained the B. Sc. degree (the M. Sc. degree is expected in the near future) in material sciences and is in charge of Ion-Plating.

None of the Centre's staff has even basic knowledge and practical experience of waste water treatment and discharge.

Waste water problems are mainly chemical and less engineering problems; in addition surface treatment engineers are generally better trained on the engineering side than on the chemical side, so that most engineering problems in waste water plants they are able to solve without extern support. So problem solving, research work and assistance to and information of the surface treatment industry preferably will happen on the chemical side, and it is an absolute condition that a waste water specialist must have excellent knowledge and practical experience in chemistry and analysis of both surface and waste water treatment. On the engineering side he needs at least some basic, but not necessarily a detailed knowledge.

These requirements direct to the necessity that a waste water specialist must be a surface treatment specialist and be assigned to the Surface Treatment Centre, Considering the education and experience of the Centre's staff Mr. Ro Byong-Ho fullfills the requirements at most; he is the only man with a broad surface treatment knowledge. He comes from Taegu and obtained the B. Sc. degree in Chemical Engineering at Inha University at Seoul. From 1979 to 1980 he spent a period in West Germany, working with a number of surface treatment companies, including Blasberg (supply house), Anke (job-plater) and Poligrat (supply house). Three years ago he went to KIST and spent his time there with troubleshooting metal finishing problems in industry. Mr. Ro joined KIMM in November, 1983, and helped a company in Pusan to reduce the incidence of pitting in the hard chromium plating of pistons used in the recoil mechanism of artillery. Since then he has collaborated with **another** staff-member on the copper-foil rig. He obtained a great deal of his chemical knowledge by education and practical work and in addition trained himself by joinig plating-chemistry courses, which he was going to finish by a final examination in May, 1985. He speaks quite reasonably English and some German.

D. Recommendations

1. Organize the Waste Water Section with KIMM, Changwon, by
   - transferring the duties and necessary freedom of action

mainly in the chemical and basic engineering field to Mr. Ro, Surface Treatment Centre,

- linking Mr. Ro's activities with the Pollution Control Group and the Chemical Analysis Laboratory which should support him on the analytical and detailed engineering side.

2. Start as soon as possible, preferably immediately, with establishing a detailed waste water work programme (for details see chapter V.B). It is estimated that Mr. Ro needs about two years of gaining practical experience and the necessary contacts to industry in order to be able to carry out efficient research and industrial support work following the lines of the Government Project.
Do not postpone the start otherwise this mission will become more or less worthless!

3. Give Mr. Ro the chance of further theoretical and practical education by attending full-day courses and working with waste water treatment companies in Korea and abroad. Consider an education of Mr. Ro in the Federal Republic of Germany, where I might be of some help to you by finding out the right courses and arranging a cooperation with a waste water supply house.

4. Consider the employment of an experienced engineer after six to twelve month after having established the Waste Water Section who may support Mr. Ro's activities with preferenc of detailed engineering.

5. Check the possibility of using the new KIMM-waste-water-treatment-plant for practical training as well as pilot plant and process testing work.

6. Chemical Analysis Laboratory: Purchase equipment for COD-single-probe-analysis, portable laboratory-fotometer, hand-test-sets and Imhoff-Cone (written information was passed on to Mr. Ro).

V. RESEARCH PROGRAMME AND CONSULTATION ACTIVITIES

A. Present situation

As already mentioned introductorily until this mission nobody of the Centre's staff had any knowledge and practical experience in waste water treatment. The training of Mr. Ro (see chapter VII) had to start from the beginning and within the given short time could just provide a basic knowledge which of course is not enough to carry out efficient and successful research work and consultation and training to industry. Furthermore there are no close contacts to the surface treatment industry giving an indication to problems in the waste water field. It is thought to be to early to start research work and as a result a research programme could not yet be suggested.

B. Recommendations

1. Repeat the subject of the training provided during this mission and continue with
   - the calculation of investment and operating expenses of the three types of waste water treatment and corresponding plants developed conceptually during the training,
   - the final selection of the most economic design of waste water treatment process and plant.
2. Apply the provided knowledge and working method to the three surface treatment complexes in Masan, Pusan and Taegu which which will come into the design stage in the near future.
3. Elaborate a survey about the surface treatment industry in Korea by
   - geographical distribution,
   - type of surface treatment like plating, painting, pickling, anodizing and others,
   - economical size,
   - water handling and waste water treatment.
4. In connection with recommendation 3. visit these companies (at least two companies per week!) whother they have problems or not, try to get practical experience and to find out their problems. Start with the plating industry thus concentrating

on one major type of waste water treatment.

5. In connection with recomendations 3. and 4. make KIMM well known as an institute where help, consultation and information can be got from.
6. Evaluate carefully the waste water problems collected by the recommended field visits and elaborate an research programme which is of interest to and financially born by the surface treatment industry.

VI. CONTACTS TO INSTITUTES AND ORGANIZATIONS ABROAD

Contacts are recommended to

1. Surface treatment organizations

in Germany:

DG Deutsche Gesellschaft für Galvanotechnik e. V.
Kreuzstraße 34
D-4000 Düsseldorf 1
Tel. 0211/132381

in the United States:

AES American Electropleters' Society
1201 Louisiana Ave.
Winter Park Florida 32789
Tel. (305) 647-1197

in the United Kingdom:

IMF Institute of Metal Finishing
Exeter House
48, Holloway Head
Birmingham B1 1NQ
Tel. 021-622-7387

2. Waste water association

in Germany:

ATV Abwassertechnische Verinigung e. V.
Markt 71
D-5205 St. Augustin 1
Tel. 02241/22005-08

The surface treatment organizations are prepared to give further information about their special activities in the waste water field, training courses, training schools and universities, special meetings and conferences and other items of interest.

VII. STAFF TRAINING

A. General

The staff training was concentrated on Mr. Ro Byong-Ho and the development of the design of a waste water treatment scheme and plant of an industrial complex of seven plating shops in Bu-Chan near Seoul. This complex was chosen because all the necessary basic plant and production data and plans were available, although its design already was established and the complex itself is under construction. So this activity and its results had pure training character.

B. Complex description

1. Site of complex: Bu-Chan near Seoul
2. Names of plating shops:
   1. Dong-Bo
   2. Sam-Sin Chem. Corp.
   3. Shin-Shin
   4. Dong-Won
   5. Yong-Bo
   6. Jung-Ang
   7. Jeong-Il
3. Types of surface Treatment and plants:
   1. Dong-Bo: Copper/Nickel/Chromium on steel (1)
      Copper/Nickel sb/Nickel b/Chromium on steel and brass (2)
   2. Sam-Shin: Electroless Copper/Electroless Nickel/ Copper/Nickel sb/Nickel b/Chromium *) on ABS-plastic material (3)
      Copper/Nickel sb/Nickel b/Chromium on steel (2)
   3. Shin-Shin: Electroless Copper/Electroless Nickel/ Copper/Nickel sb/Nickel b/Chromium on ABS-plastic material (3)
      Copper/Nickel/Chromium on steel (1)
   4. Dong-Won: Electroless Copper/Electroless Nickel/ Copper/Nickel sb/Nickel b/Chromium on ABS-plastic material (3)
      Copper/Nickel/Chromium on steel (1)

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*) sb = semibright; b = bright;

5. Yong-Bo:	Nickel sb/Nickel b/Chromium on steel	(2a)
	Nickel sb/Nickel b on steel (barrel-plating)	(2b)
	Zinc (acid) on steel (barrel-plating)	(4)
	Zinc (cyanide) on steel	(5)
6. Jung-Ang:	Nickel sb/Nickel b/Chromium on steel and brass	(2a)
	Zinc (cyanide) on steel	(5)
	Zinc (acid) on steel (barrel-plating)	(4)
	Nickel on steel (barrel-plating)	(1a)
7. Jeong-Il:	Electroless Copper/Electroless Nickel/Copper/Nickel sb/Nickel b/Chromium on ABS-plastic material	(3)
	Copper/Nickel on zinc die-castings (barrel-plating)	(6)
	Nickel on steel (barrel-plating)	(1a)

From the plant description it is seen, that all seven companies use some of six main types of treatment and plants (numbers in bracketts 1 - 6); further three minor types can be regarded as sections of the main types 1 and 2 (numbers 1a, 2a and 2b). So the waste water calculation work could be restricted to nine plant-types.

C. Design development

The design development includes the following steps:

- description of plating production,
- calculation of annual amount of waste water and its chemical/product load of each plating plant,
- calculation of annual amount of waste water and its chemical/product load of each plating shop,
- calculation of annual amount of waste water and its chemical/product load of the total complex,
- calculation of the chemical/product load of the flowing water of the total complex - evaluation for circulation,
- calculation of data of an ion-exchange plant and filter-press equipment,
- designing the various possible treatment and plant schedules.

Description of plating production - status figures

The description of the plating production on the basis of given production data and plans has to be prepared as detailed as possible following a special scheme. Important data are sequence of plating-tanks, bath-volume, type, composition and temperature of electrolytes or solutions, process sequences, types and amounts of replenished chemicals/products, frequency of replenishments, frequency of bath disposal, flow-rinsing speed, dragg-out volume, production through-put and working time. Annex 1 shows one of the prepared nine survey-tables, here the copper/nickel/chromium-plant of Dong-Bo. All important status-figures are given in columns 1 - 21 and in the head of the table.

(Remark: In this report only samples of the extensiv paperwork developed during the staff-training are shown; the whole work remained with Mr. Ro at IMM).

In the case of designing not only the waste water treatment concept, but also the production plants, figures of replenishments (amounts of chemicals/products, frequency) and bath service life (frequency of disposal) are not yet available; they have to be found by calculation under certain assumptions (see next subsection) or fixed by practical plating experience.

Calculation of wast water amount and load of each plant

On the basis of the status figures described above now the annual amount of waste water and its load by chemicals/products had to be calculated; in detail these figures include the annual amount of chemicals/products used and brought into the waste water at each bath of the plant, the annual amount of waste water concentrates (process electrolytes and solutions discharged) and half-concentrates (stand-rinsing water discharged) of each bath separated in the various necessary waste water treatment branches and the annual consumption of flowing (flow-rinsing) water divided into the non-cyanide- and cyanide-containing branch. These results are shown, once again as an example, in columns 22 - 29 of annex I, and comments are given in column 30.

The calculation formula used are developed and described in detail in annex 2. Usually this type of calculation is done by electronic data processing; during this training the work had to be done by hand-calculators. All formula were developed and explained carefully during their application; in some cases where the calculations started to become too time-consuming approximate solutions had to be used in order to proceed.

In the case of bath replenishments the amount of replenished chemicals/products were calculated on the premises that

- the amount of chemicals/products to be replenished is equal to the dragg-out losses within a period between two replenishments,
- in the case of metal deposition the metal concentration change causedby different anode- and cathode efficiency is neglected,
- in cyanide solution the displacement of cyanide by carbondioxide resulting in an increased cyanide consumption and replenishment is neglected,
- evaporation with or without sucking-off systems is neglected (influence on bath concentration is as low as 1 % and less).

The frequency of bath discharge was fixed by experience.

Calculation of waste water amount and load of each plating shop

The annual waste water figures calculated for each plant were now added up for each plating shop and combination of plants given there. The results, once again in the case of Dong-Bo, are given in annex 3. Lines 5 - 9 show, that Dong-Bo produces

- 358 m^3/a waste water, which has to be neutralized,
- 514 m^3/a waste water containing hexavalent chromium, which has to be depoisoned by reduction,
- 33 m^3/a degreasing concentrates and halfconcentrates, which cause difficulties during waste water treatment and because of this have to be treated in a special emulsion-breaking step,
- 6,360 m^3/a cyanide-free flow-rinsing water,
- 1,200 m^3/a cyanide-containing flow-rinsing water, which has to be depoisoned by oxidation.

The chemical/product load figures of these waste water shares are

are given in columns 10 - 45 , line 6 - 9, of annex 3. They permit a conclusion on a possible unefficient use of chemicals/products in production (too much or frequent replenishments, too frequent discharges) and the need of chemicals for waste water treatment.

Calculation of waste water amount and load of the total complex

The annual waste water amount and chemical/product load of each plating shop were now summed up to the total complex figures; these are shwon in annex 4. According to this the waste water treatment plant of the complex has to treat annually

- 5.415 m^3/a concentrates and halfconcentrates by neutralization;
- 130 m^3/a cyanide containing concentrates and halfconcentrates by oxidation of the cyanide;
- 1.449 m^3/a concentrates and halfconcentrates containing hexavalent chromium, which has to be depoisoned by reduction;
- 243 m^3/a degreasing concentrates and halfconcentrates by emulsion-breaking and neutralization;
- 20 m^3/a palladium-containing concentrates; the palladium has to be recycled by ion-exchange, the solution then to be neutralized;
- 60 m^3/a electroless nickel concentrates and halfconcentrates; this waste water share either has to be discharged by external facilities or the harmful influence of complexing agents like ammonia must be overcome by precipitating nickel at high pH-value, filtering-off the nickelhydroxide and discharging the filtrate separately from the main share of waste water;
- 30 m^3/a potassiumthiocyanate contaring concentrates and halfconcentrates, which have to be depoisoned by oxidation like cyanide or discharged externally;
- 62,310 m^3/a cyanide-free flowing(flow-rinsing) water, which has to be neutralized or might be cleaned by ion-exchange and circulated back to the plant; a share of 4,800 m^3/a has to be used in the deionized con-

	dition because of quality reasons (very clean rinsing of the surface treated products in the final rinsing step);
- 6,510 m^3/a	cyanide-containing flowing(flow-rinsing) water, which has to be depoisoned by cyanide-oxidation or cleaned by ion-exchange; in the latter case it will be circulated back to the production plant.
- 7,347 m^3/a	Total annual amount of concentrates and halfconcentrates to be treated as described above,
-68,820 m^3/a	Total annual amount of flowing(flow-rinsing) water as to be treated as the concentrates and halfconcentrates or to be cleaned by ion-exchange and then circulated back to the production plant.

The load of chemicals/products of each waste water share above once again is given in columns 10 - 45, lines 9 - 18, of annex 4. Special attention should be drawn to the high load of the flowing water (line 10) by nearly every type of chemical/product; this will be regarded and discussed more in detail below.

Calculation of the chemical/product load of the flowing water - Evaluation for circulation

There are two basic technical principles of waste water treatment (for more details see VIII. Seminar presentation):

- The flowing-through technique: all the waste water (concentrates, halfconcentrates and flow-rinsing water) is treated in the waste water plant while flowing-through continuosly.
- The batch-technique: the waste water share with high load of chemicals/products (concentrates and halfconcentrates) is treated batch-wise, whereas the flow-rinsing water with a low chemical/product load is circualted back to the plating plants via an ion-exchange plant for continuos deionizing.

The introduction of an flow-rinsing circuit reduces water consumption at least by 90 - 95 %. The grade of its contamination by chemicals and products, however, must not exceed 4 mval/l (i. e.

4 val/m^3), otherwise the regeneration of the ion-exchange resins will becom to frequent and unefficient.

In the present case as a next step of waste water treatment design development it has to be checked whether the load of the 68,820 m^3/a flowing water exceeds 4 mval/l. For this purpose the annual load of each chemical/product, shown in lines 9 - 11 of annex 4, has to be transferred into val and then summed up to an annnual total. The results of this calculation are shown in the following tables 1, 2 and 3 for the non-cyanide flowing water and its deionized share of 4,300 m^3/a as well as the cyanide-containing flowing water. In all three cases the limit of 4 mval/l is extremely exceeded; this is due to heavy drag-in of chemical/product from the process-electrolytes and solutions straight into the flow-rinsing water without for example prior stand-rinsing step which would keep back 70 - 90 % of the load. Under these circumstances in none of the three cases a flow-rinsing circuit is efficient and advisable. If it should be introduced, at first the rinsing situation in the plating plants has to be improved by introducing suitable rinsing techniques like stand- or spray-rinsing prior to flow-rinsing or recycling techniques at single process-steps. An other way to reduce load is just to reduce concentration of process solutions like etching, pickling or degreasing solutions, so that also drag-outs are minimized.

Calculation of data of an ion-exchange plant and filter-press equipment

Although in the present case flow-rinsing circuits would not work efficiently, for training purposes the calculation of ion-exchange plant data for the non-cyanide circuit was carried out. The results are shown in table 4 below; they supply the basic size data for plant construction and moreover certify the low efficiency of this circuit given by a high number of necessary regenerations connected with high chemical consumption and total eluation water amount. The total annual water saving is somewhat less than 90 %.

The filter-press data were taken from data-tables in Taschenbuch der Abwasserbehandlung (Dr. L. Hartinger, Carl Henser Verlag, München, 1977), page 656/657 as follows:

<u>Table I</u> Annual load of non-cyanide flowing water
Total water amount: 57.510 m^3/a

Chemical/product	Annual load		Annual load of flowing water	
			Kations	Anions
	kg/a	val/kg	val/a	val/a
1	2	3	4	5
HCl 30-33 %	30188	8.62		260220
HNO_3 65 %	1098	10.47		11490
H_2SO_4 96 %	90693	15		1360395
NaOH	343	25	8575	
NH_4OH 25 %	141	14.68	2070	
$ZnCl_2$	2793	14.68	40980	40980
NH_4Cl	6423	18.7	120100	120100
Cu-Pyrophosphate	376	6.65	2500	2500
K-Pyrophosphate	1368	3.97	5400	5400
$CuSO_4 \cdot 5H_2O$	8709	8	69670	69670
$NiSO_4 \cdot 6H_2O$	9168	7.61	69800	69800
$NiCl_2 \cdot 6H_2O$	1792	8.41	15000	15000
H_3BO_3	1138	48.54		55200
Na-Citrate	2840	8.4	23800	23800
Na-Hypophosphite	1140	9.43	10750	10750
KSCN	9	10.29	92	92
Rochelle-salt	9	7.09	63	63
CrO_3	18632	10		186300
Dia-Cr-NC CrO_3	6066	10		59440
Na_2F_2		23.8	2900	2900
Ul-202 CrO_3	1542	10		15420
Ul-10 CrO_3	772	10		1600
Na_2SiF_6		10.63	100	100
AT-64 CrO_3	834	10		8340
ST-10 Na_2F_2	1040	23.8	24750	24750
7 degreasing products	13565	7 salt 6 NaOH	94955 81390	94955
Total val/a			572895	2439265
Total mval/l			9.96	42.41

<u>Table 2</u> Annual load of cyanide-containing flowing water
Total water amount: 6.510 m^3/a

Chemical/product	Annual load		Annual load of flowing water	
			Kations	Anions
	kg/a	val/kg	val/a	val/a
1	2	3	4	5
NO-200 NaCN 20 %	968	20.41	4000	4000
NaOH 80 %		25	19360	
ZnO	568	24.57	13950	13950
NaOH	154	25	3850	
CuCN	1491	11.16	16640	16640
NaCN	4859	20.41	99170	99170
KSCN	144	10.29	1480	1480
Rochelle-salt	434	7.09	3070	3070
Brass-salt CuCN	440	11.16	2700	2700
$Zn(CN)_2$		17.04	2050	2050
NaCN		20.41	1640	1640
Total val/a			167910	144700
Total mval/l			25.79	22.23

<u>Table 3</u> Annual load of flowing water deionized for high-quality rinsing
Total water amount: 4.800 m^3/a

Chemical/product	Annual load		Annual load of flowing water	
			Kations	Anions
	kg/a	val/kg	val/a	val/a
1	2	3	4	5
H_2SO_4 96 %	18412	15	-	276180
CrO_3	20968	10	-	209680
Total val/a			-	485860
Total mval/l			-	101.22

Table 4 Technical data ion-exchange plant - Non-cyanide circuit

Technical data	Dimension	Kations	Anions
1	2	3	4
Circuit water load	val/a	572895	2439265
Circuit water amount	m^3/a	57510	
Specific capacity	m^3/h	20	
Specific load	mval/l	9.96	42.41
		(preferably 2 - 4)	
Specific resin capacity	val/l	1 (strong acid)	0.8 (medium basic)
Total resin capacity	l/a	573000	3050000
Number of regenerations	1/a	100 (2/week)	300 (daily)
Actual resin volum	l	5730	10160
Number of resin columns	-	4	7
Column-volume	l	1500	1500
Load of column (spec. capacity/ column-volume)	l/h	13.33 (preferably 5 - 40)	
Specific eluation amount	l/l_{Resin}	12	7
Chemical consumption (theory value = 100 %)	%	120 - 130	
Amount of eluation per regeneration	m^3	18	10.5
Annual amount of eluation water	m^3/a	1800	3150
Number of gravel-filter rinsings	1/a	100	
Annual amount of gravel-filter rinsing water	m^3/a	500 - 1000	
Chemical consumption for resin regeneration:			
Hydrochloric acid (30-33 %)	kg/a	83000	
Sodiumhydroxide-solution (50 %)	kg/a		244000
Total waste water amount produced by regeneration and rinsing (gravel-filter)	m^3/a	about 6000	
Water reduction by circuit	m^3/a	57510 - 6000 = 51500	
	%	89.6	

- Plant capacity: 10 m^3/h	Filter-plate size	1200 x 1200 mm^2
	Total filter area	178 m^2
	Number of filter-plates	70
- Plant capacity: 0.5 - 1.0 m^3/h		
	Filter-plate size	500 x 500 mm^2
	Total filter area	5 - 10 m^2
	Number of filter-plates	12 - 20

Designing the various possible treatment and plant schedules

As already mentioned earlier waste water treatment can be carried out by either the flowing-through technique or the batch technique (for details see VIII. Seminar presentation). A third possibility is a combination of flowing-through treatment of the flowing water with batch treatment of concentrates and halfconcentrates. So on the next pages three treatment designs are developed:

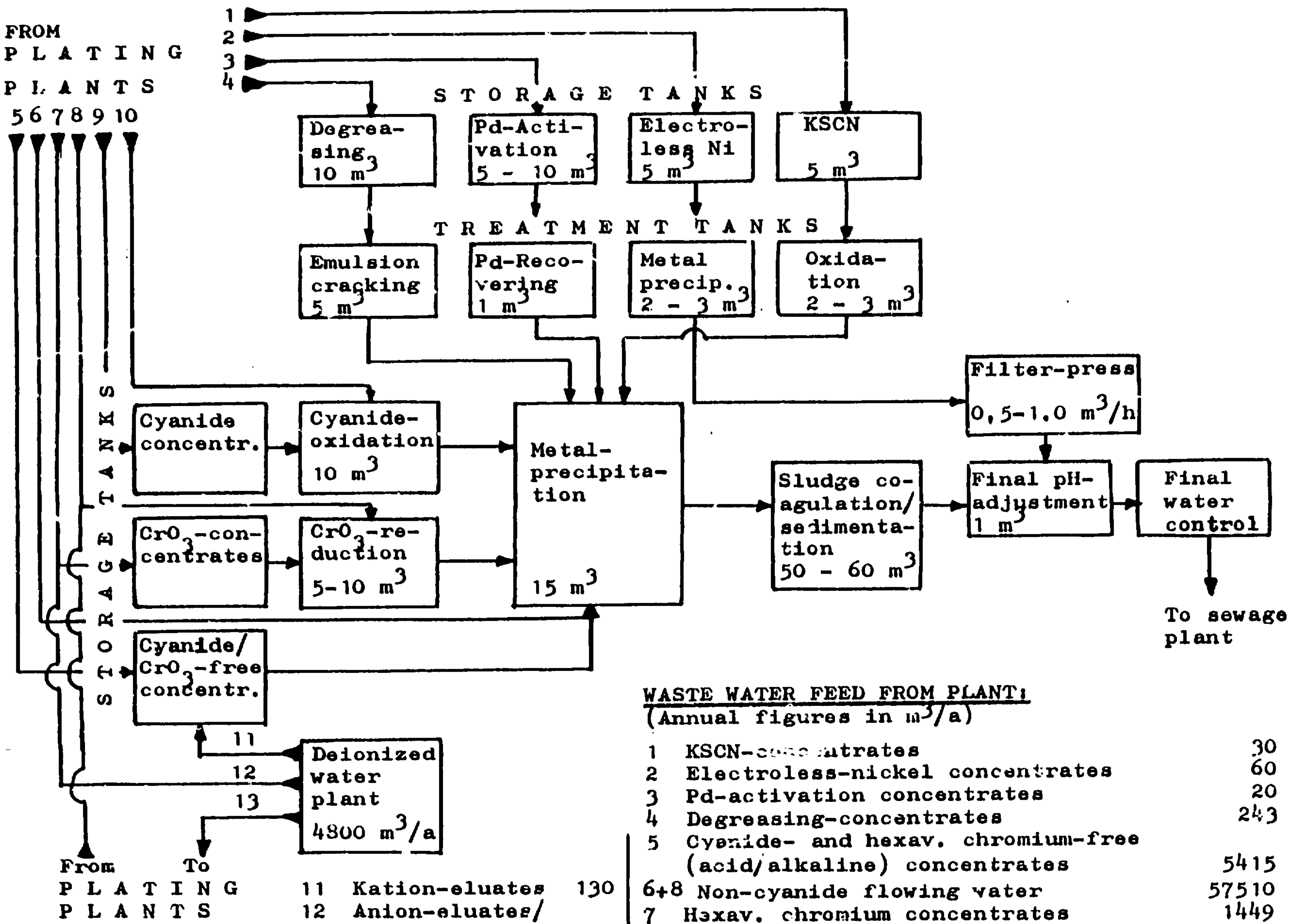
- Design 1: Flowing-through technique (concentrates, halfconcentrates, flowing water) without flow-rinsing circuit;
- Design 2: Batch treatment (concentrates, halfconcentrates) with two flow-rinsing circuits:
  - non-cyanide flow-rinsing water,
  - cyanide-containing flow-rinsing water;
- Design 3: Flowing-through treatment of the flowing water share and batch treatment of the concentrates and halfconcentrates without flow-rinsing circuits.

(The expression "concentrate" in the three schedules on pages 26 - 28 includes also halfconcentrates!).

Evaluating and selecting the optimum solution for the present case one has to observe that

- the chemical/product load of the flowing water is too high for an efficient operation of a flow-rinsing circuit. The load itself cannot be reduced remarkably by improving the rinsing technique because a corresponding supplement and change of the plating plants is not longer possible.

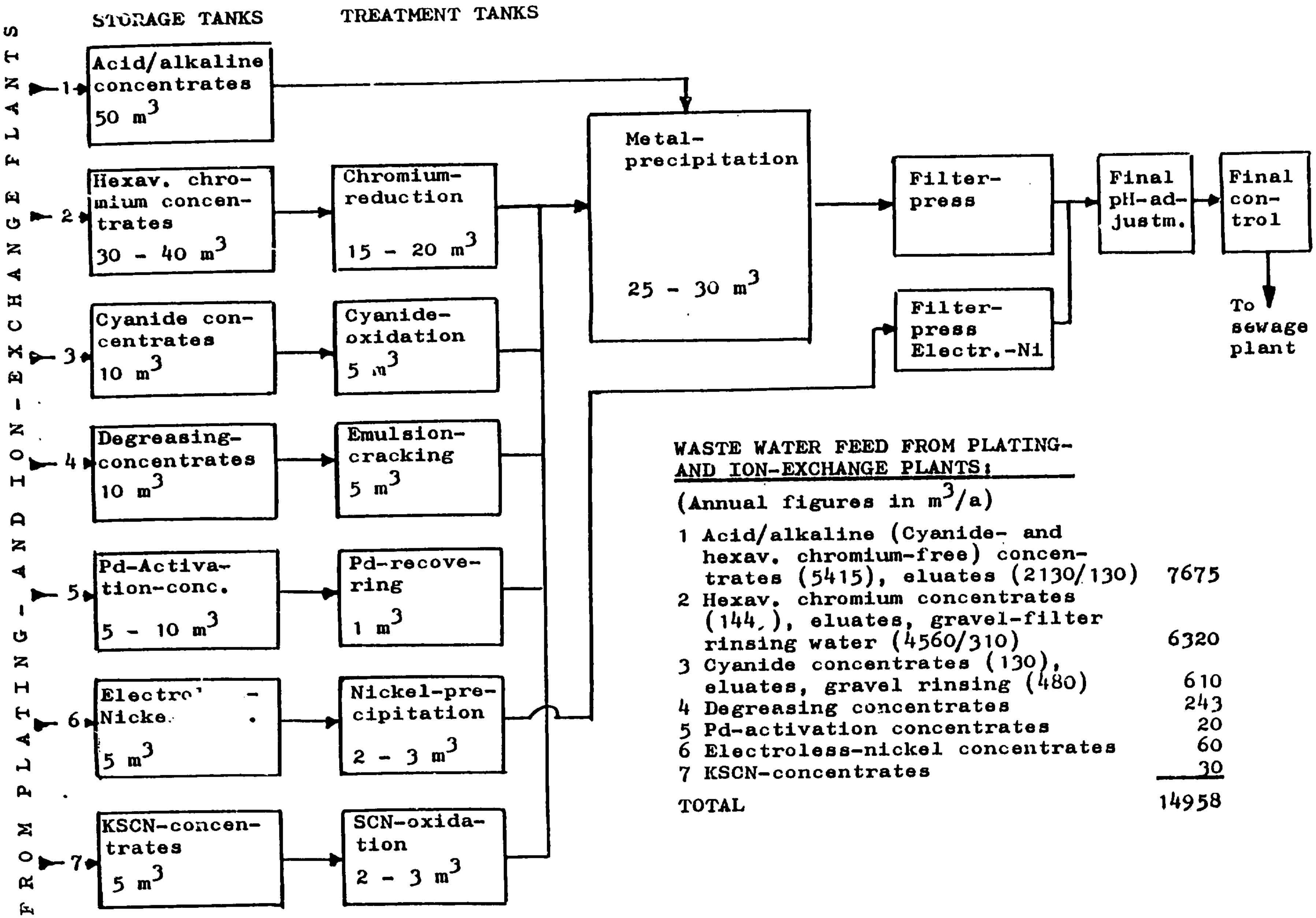
DESIGN 1: Waste water flowing-through treatment without flow-rinsing circuits



11	Kation-eluates	130
12	Anion-eluates/ gravel rinsing	310
13	Deionized feed	4800
Total		5240

WASTE WATER FEED FROM PLANT:
(Annual figures in m^3/a)

1	KSCN-concentrates	30
2	Electroless-nickel concentrates	60
3	Pd-activation concentrates	20
4	Degreasing-concentrates	243
5	Cyanide- and hexav. chromium-free (acid/alkaline) concentrates	5415
6+8	Non-cyanide flowing water	57510
7	Hexav. chromium concentrates	1449
9	Cyanide-concentrates	130
10	Cyanide-containing flowing water	6510
Total		71367



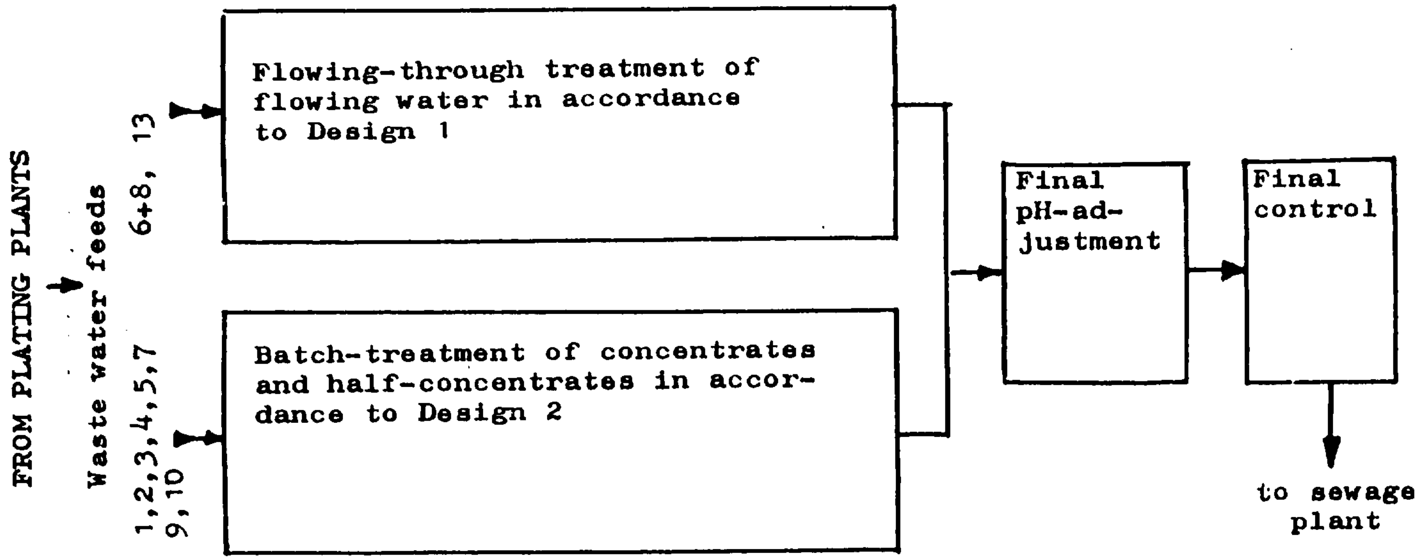
WASTE WATER FEED FROM PLATING- AND ION-EXCHANGE PLANTS:

(Annual figures in m^3/a)

1	Acid/alkaline (Cyanide- and hexav. chromium-free) concentrates (5415), eluates (2130/130)	7675
2	Hexav. chromium concentrates (144,), eluates, gravel-filter rinsing water (4560/310)	6320
3	Cyanide concentrates (130), eluates, gravel rinsing (480)	610
4	Degreasing concentrates	243
5	Pd-activation concentrates	20
6	Electroless-nickel concentrates	60
7	KSCN-concentrates	30
	TOTAL	14958

DESIGN 2: Waste water batch-treatment with flow-rinsing circuits

DESIGN 3: Combination of batch- and flowing-through treatment without flow-rinsing circuits



WASTE WATER FEED FROM PLATING PLANTS:

(Annual figures in m^3/a)

1 KSCN-concentrates	30
2 Electroless-nickel concentrates	60
3 Pd-activation concentrates	20
4 Degreasing concentrates	243
5 Cyanide- and hexav. chromium (acid/alkaline) concentrates *)	5545
6 Hexav. chromium concentrates *)	1759
9 Cyanide-concentrates	130
6+8 Non-cyanide flowing water	57510
10 Cyanide-containing flowing water	6510
13 Deionized high-quality-rinsing water	4800
Total	76607

*) including 130 resp. 310 eluates and gravel rinsing water from deionizing plant

- the batch treatment offers advantages and treatment reliability especially in the case of concentrates and halfconcentrates which very often cause trouble in flowing-through treatment.

Considering these points it has to be concluded that design 3 offers the best solution of waste water treatment of the Bu-Chan complex from the technical point of view; the economic side has not yet been considered (see recommendation 1 on page 13) (It is not known, what type of waste water treatment actually is being realized in Bu-Chan!).

Literature and written information

During staff training copies and commercial prospects were provided to Mr. Ro of all important written informations and papers concerning the single sections of the training. Furthermore all calculations, elaborated tables und surveys not annexed to this report by space reasons were left to him as a basis for further work.

VIII. SEMINAR PRESENTATION

During the mission two papers were prepared and presented:

1. Waste Water Treating Technology in Metal Finishing Processes. (Special Seminar presented at the Academic Meeting of the Korea Metal Finishing Society at Taegu, May, 4th, 1985).
2. Environment Pollution Control in the German Surface Finishing Industry. (Presented at the Annual Meeting of the Environment Control Engineers of the Chang-Won Industrial Complex at Chang-Won (City-Hall) May, 8th, 1985).

Both papers are annexed to this report in full wording (annexes 6 and 7).

IX. FIELD VISITS

Two visits were paid on May, 6th, 1985 to Ban Weol Electroplating Industry Corp., Ban Weol-Myon, and Kyung-In Electroplating Corp., Ban Weol-Myon, both near Seoul. For details see visit report enclosed as annex 5. An over-all impression was that the waste water treatment scheme is more complicated than necessary; this might be due to endeavouring to overcome difficulties caused by improper waste water handling in the electroplating shops, but a second reason might be that the Japanese treatment scheme and plants, which are necessary to meet the Japanese specifications, offer more than in Korea is required. In order to save investment costs (foreign currency) and operation expenses this point should be checked and considered carefully in the future.

X. RECOMMENDATION (SUMMARY)

Recommendation	to	for details see page
1. Check justification and efficiency of one-month's-missions	UNIDO	7
2. Organize the Waste Water Treatment Section	KIMM, STC*)	11
3. Start as soon as possible, do not postpone the start too long!	KIMM, STC	12
4. Establish a waste water work programme:	KIMM, STC, WWS*)	12
4.1 Repeat the subject of the training provided during this mission	KIMM, WWS	13
4.2 Apply the provided knowledge and working method to the three future complexes in Masan, Pusan and Taegu	KIMM, WWS	13
4.3 Elaborate survey about surface treatment industry in Korea	KIMM, WWS	13
4.4 Pay field visits to this industry (at least two visits per week!)	KIMM, WWS	13
4.5 Make KIMM well-known as an institute where help, consultation and information can be got from.	KIMM, WWS	14
4.6 Evaluate collected waste water problems and elaborate research programmes.	KIMM, WWS	14

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*) STC = Surface Treatment Centre; WWS = Waste Water Section;

Recommendation (contd.)	to	for details see page
5. Give chance of further theoretical and practical education in Korea and abroad	KIMM, STC	12
6. Consider the employment of an experienced engineer after six to twelve months	KIMM, STC	12
7. Check the possibility of using the new KIMM-waste-water-treatment plant for training and testing work	KIMM, STC/ PCG*)	12
8. Purchase recommended laboraty equipment for waste water analysis	KIMM, CAL*)	12
9. In all cases of waste water treatment plant offers check carefully whether the plant meets exactly the requirements and is neither too small nor too big	KIMM, STC	30

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*) PCG = Pollution Control Group;
CAL = Chemical Analysis Laboratory.

ORIGIN OF WASTE WATER - ANNUAL FIGURES OF WASTE WATER AMOUNT AND CHEMICAL LOAD

PLATING SHOP: [illegible]-[illegible], [illegible] near Seoul

PLANT: Copper/Nickel/Chromium onto Steel
Brass onto Steel
Black-Nickel onto Steel

THROUGH-PUT: Cu/Ni/Cr-Steel 30 charges/day 120 dm²/charge 36 m²/day
Cu/Ni/Black-Ni-Steel 20 charges/day 80 dm²/charge 37 m²/day
Cu/Ni/Brass-Steel [illegible] charges/day [illegible] dm²/charge 37 m²/day
Total 70 charges/day [illegible] m²/day

DRAG-OUT LOSSES: 0.13 l/m² or 0.13 l/charge

WORKING HOURS: 10 hrs/day, 6 days/week, 50 weeks/year

STATUS - FIGURES															CALCULATED ANNUAL FIGURES									COMMENTS
Pos.	Type of treatment	Bath-volume	Chemicals/Products Type	Temp.	Conc.	Process sequence Cu/Ni/Cr-Steel	Cu/Ni/BlNi-Steel	Cu/Ni/Brass-Steel	Chemicals/Products replenished Type	Amount	Frequency	[illegible]	[illegible]	Flow-rinsing	Chem. Products See 1)	Waste Water Sulfate/Concentrate	[illegible]	[illegible]	[illegible]	[illegible]	Flowing-water [illegible]	[illegible]	
No.		l		°C	g/l					kg				m³/h	kg/a	m³/a	m³/a	m³/a	m³/a	m³/a	m³/a	m³/a	
1	2	3	4		5	6	7	8	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
1	Loading					1	1	1															
2	Rinsing	800	Tapwater			3	3	3				p	30m		430 [illegible]								
3	Degreasing electrol.	1630	[illegible]	30	80	2	2	2	[illegible]	10	w	p o	4m		307	3.6							
4 -5	Flow-rinsing cascade from 5 to 4	1600	Tapwater from Pos. 7			4 5	4 5	4 5						0.2	91 [illegible]								
6	Pickling	800	Sulfuric acid 10 %		100	6	6	6				p	30m		3763	[illegible]							
7 -8	Flow-rinsing cascade from 8 to 7	1600	Tapwater to Pos. 5			7 8	7 8	7 8						0.2	1433	H_2SO_4					400		
9	Striking electrol.	1630	Coppercyanide solution copper(I)cyanide sodiumcyanide	30	 30 40	9	9	9	copper(I)cyanide sodiumcyanide	4.2 3.6	2w												
10	Rinsing	800	Tapwater from Pos. 11			10	10	10				p See comm.	12m		26 36	CuCN NaCN	9.6						200 l/d returned to 9, replenished from 11
11 -12	Flow-rinsing cascade from 12 to 11	1600	Tapwater partly to Pos. 10			11 12	11 12	11 12						0.1	79 103	CuCN NaCN						300	
13	Neutralization	800	Sulfuric acid 10 %		100	13	13	13				p	30m		3763	[illegible]							
14	Flow-rinsing	800	Tapwater from Pos. 16			14	14	14						0.3	1433	H_2SO_4							
15	Copperplating (acid)	2000	Coppersulfate-electrolyte coppersulfate sulfuric acid additives 2 ml/l	25	 200 60 2	15	15	15	coppersulfate sulfuric acid additives	33 10 by [illegible]	w												coppersulfate as $CuSO_4 \cdot 5H_2O$
16 -18	Flow-rinsing cascade from 18 to 16	2400	Tapwater from Pos. 20 to Pos. 14			16 17 18	16 17 18	16 17 18						0.3	1730 325	$CuSO_4 \cdot 5H_2O$ H_2SO_4							
19	Pickling	800	Sulfuric acid 10 %		100	19	19	19				p	30m		3763	[illegible]							
20	Flow-rinsing	800	Tapwater to Pos. 18			20	20	20						0.3	1433	H_2SO_4					900		
21	Bright-nickelplating	2000	Watts-solution nickelsulfate nickelchloride boric acid additive [illegible] 12 ml/l additive [illegible] 1.2 ml/l	55	 280 45 40 12 1.2	21	21	21	nickelchloride boric acid sulfuric acid	33 3 1.3	w w d												nickelchloride as $NiCl_2 \cdot 6H_2O$ sulfuric acid to compensate nickelsulfate drag-out of 20.7 kg/week
22	Rinsing	800	Tapwater from Pos. 23			22	22	22				p See comm.	12m		63.3 30.3	$NiSO_4 \cdot 6H_2O$ $NiCl_2 \cdot 6H_2O$	9.6						200 l/d returned to 21, replen. from 23
23 -24	Flow-rinsing cascade from 24 to 23	1600	Tapwater partly to Pos. 22			23 24	23 24	23 24						0.15	[illegible] 722.6 [illegible] [illegible]	H_3BO_3 $NiSO_4 \cdot 6H_2O$ $NiCl_2 \cdot 6H_2O$ H_3BO_3					450		
25	Black-Nickel	1630	- nickelsulfate nickelchloride ammoniumchloride zincchloride [illegible]-salt potassiumthiocyanate	30	 67 67 22 13 11 11		25		nickelsulfate nickelchloride ammoniumchloride zincchloride [illegible]-salt potassiumthiocyanate	1 1 0.33 0.23 0.17 0.17	2w												nickelsulfate as $NiSO_4 \cdot 6H_2O$
26	Rinsing	800	Tapwater				26					p See comm.	12m		See 2)				9.6				100 l/d returned to 25, replen. from 27
27 -28	Flow-rinsing cascade from 28 to 27	1600	Tapwater partly to Pos. 26				27							0.12	See 3)						360		
29	Brassplating	1630	- brass-salt (total of 30 g/l)	40	 150			25	Brass-salt Brass-salt	5.2	2w												
30	Rinsing	800	Tapwater from Pos. 31					26				3p See comm.	4m		26	Brass-salt	3.8						200 l/d returned to 29, replen. from 31
31 -32	Flow-rinsing cascade from 32 to 31	1600	Tapwater partly to Pos. 30					27 28						0.12	700	Brass-salt						360	
33	Antitarnishing	1630	AT-[illegible]-solution AT-[illegible] 200 ml/l (Cr(VI) 20 g/l)	25	200			29				3m	4m		743	AT-[illegible]	3.8						
34	Flow-rinsing	800	Tapwater					30						0.1	417	AT-[illegible]					300		
35	Chromiumplating	1630	[illegible]-Cr-[illegible]-solution chromic acid sulfuric acid	45	 100 0.[illegible]	25			chromic acid sulfuric acid	6 0.07	w												
36 -37	Rinsing	1600	Deionized water			26 27						o See comm.	12m		137	CrO_3	19.2						
38 -40	Flow-rinsing cascade from 40 to 38	2400	Tapwater			28 29 30								0.03	62	CrO_3					150		30 l/h returned to 35, repl. from 37
41	Unloading					31	28	31															

Further comments:
1) Type of chemical product see column 4 or 16, if not immediately following the kg/a-figure.
2) 6.8 kg $NiSO_4 \cdot 6H_2O$
6.8 kg $NiCl_2 \cdot 6H_2O$
2.3 kg NH_4Cl
1.5 kg $ZnCl_2$
1.1 kg [illegible]-salt
1.1 kg KSCN
3) 18.6 kg $NiSO_4 \cdot 6H_2O$
18.6 kg $NiCl_2 \cdot 6H_2O$
6.1 kg NH_4Cl
4.3 kg $ZnCl_2$
3.1 kg [illegible]-salt
3.1 kg KSCN

MATHEMATICAL FORMULA
used for the calculation of drag-out losses

A. Survey about drag-in/drag-out combinations and evaluation of practical cases

—		DRAG-IN		
		None	Water	Water + Stuff
DRAG-OUT	None	-	-	-
	Water	-	-	-
	Water + Stuff	(4)	(7)	(14) and (16)

For the case being at hand only the following three combinations are of practical interest:

Drag-out of water + stuff (i. e. process electrolyte, rinsing or other solutions)

with prior

- none drag-in (first step of treatment like degreasing, where the parts are immersed in dry condition),
- drag-in of just water (first step of a treatment section, where the carefully rinsed parts drag-in just pure rinsing water),
- drag-in of water + stuff (the normal case of dragging-over solution from bath to bath within a treatment section).

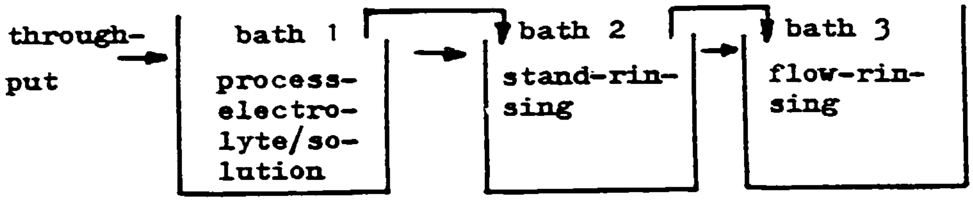
A treatment section consists of a group of treatment bathes beginning with the process electrolyte/solution, which is followed by a group of rinsing bathes.

In the survey-table above the numbers in brackets refer to the mathematical formula described in detail below and to be applied for the drag-in/drag-out combination concerned.

B. Calculation Formula

Prior conditions

1. The treatment section consists of three bathes



2. The stuff (chemical/product) in bath 1 is not recovered by adding fresh products or dragging-in from a bath before.
3. In bath 2 there is no share of flowing water at all.
4. Drag-in volume is equal to drag-out volume; they furthermore are assumed to be independant on viscosity of the variuos types of electrolytes or solutions.
5. In bath 3 the flow-rinsing efficiency is 100 %; from there no stuff is dragged-out into the next treatment section.

Abbreviations

As abbreviations are used

c = concentration of stuff regarded in g/l

V = volume of bath regarded in l

M = mass of stuff in the bath regarded ($M = c \cdot V$) in g

VDA = drag-out volume in l

n = number of charges treated in the section concerned within the service life of bath 1 or within the period between two stuff-replenishments of bath 1.

V is indexed by the number of bath regarded (i. e. V_1 = volume of bath 1); c and M are indexed twice, the first index referring to the number of charges and the second to the number of bath regarded. So for instance c_{01} = concentration of bath 1 after zero charges throughput, M_{n1} = mass of stuff in bath 1 after n charges throughput.

Calculation formula

Additional prior condition: No recycling from bath 2 to bath 1.
Combination: No drag-in/Water + stuff drag-out

In bath 1 concentration c stays constant until the dragged-out volume is replenished by water (which happens daily until weekly once). The number of charges treated in bath 1 between two water-replenishments is m, the number of replenishment periods within the service life of bath 1 or within the period of two stuff-replenishments of bath 1 is z. So it follows

$$n = m \cdot z \tag{1}$$

The development of concentration as a function of through-put (number of charges) is as follows:

c_{01} during charge numbers 1 until m
$c_{m+1\,1}$ during charge numbers m + 1 until 2m
$c_{2m+1\,1}$ during charge numbers 2m + 1 until 3m
.
.
.
$c_{(z-1)m+1\,1}$ during charge numbers (z-1)m + 1 until zm

The final concentration $c_{(z-1)m+1\,1}$ after zm = n charges is given by

$$c_{(z-1)m+1\,1} = c_{01} \left(1 - \frac{m \cdot VDA}{V_1} \right)^z \tag{2}$$

The resting stuff in bath 1 after n charges follows from (2) by

$$M_{(z-1)m+1\,1} = c_{(z-1)m+1\,1} \cdot V_1$$

giving

$$M_{(z-1)m+1\,1} = c_{01} \cdot V_1 \left(1 - \frac{m \cdot VDA}{V_1} \right)^z \tag{3}$$

and the stuff-mass dragged-out from bath 1 into bath 2 follows from the mass-balance

$$M_{(z-1)m+1\,1 \rightarrow 2} = c_{01} \cdot V_1 - M_{(z-1)m+1\,1}$$

to

$$\boxed{M_{(z-1)m+1\,1 \rightarrow 2} = c_{01} \cdot V_1 \left[1 - \left(1 - \frac{m \cdot VDA}{V_1} \right)^z \right]} \tag{4}$$

Combination: Water drag-in/Water + stuff drag-out

In this case the water volume dragged-in by each charge replenishes the dragged-out volume; the total bath volume stays constant and m = 1, so that follows n = z. The formula (2), (3) and (4) now can be written as follows:

Final concentration after n charges through-put through bath 1

$$(5) \qquad c_{n1} = c_{01} \left(1 - \frac{VDA}{V_1} \right)^n$$

Resting stuff in bath 1 after n charges

$$(6) \qquad M_{n1} = c_{01} \cdot V_1 \left(1 - \frac{VDA}{V_1} \right)^n$$

Stuff-mass dragged-out from bath 1 into bath 2

$$(7) \qquad \boxed{M_{n1 \rightarrow 2} = c_{01} \cdot V_1 \left[1 - \left(1 - \frac{VDA}{V_1} \right)^n \right]}$$

Combination: Water + stuff drag-in/water + stuff drag-out
The next step is the calculation of the resting stuff-mass in bath 2 from the balance of dragged-in stuff minus dragged-out stuff. After the first charge put through bath 2 the balance is

$$(8) \qquad M_{12} = c_{01} \cdot VDA - c_{12} \cdot VDA + M_{02}$$

Normally stand-rinsing in bath 2 is started with plain water, i. e. $M_{02} = 0$, but by reason of completeness M_{02} here will not be neglected. The concentration c_{12} follows from

$$(9) \qquad c_{12} = (M_{02} + c_{01} \cdot VDA)/V_2$$

After the second charge the balance is

$$(10) \qquad M_{22} = M_{12} + c_{11} \cdot VDA - c_{22} \cdot VDA$$

with

$$(11) \qquad c_{22} = (M_{12} + c_{11} \cdot VDA)/V_2$$

Replacing c_{22} by (11) and M_{12} by (8) equation (10) gets the final form of

$$(12) \qquad M_{22} = M_{02}\left(1 - \frac{VDA}{V_2}\right)^2 + c_{01} \cdot VDA\left(1 - \frac{VDA}{V_2}\right)^2 + C_{11} \cdot VDA\left(1 - \frac{VDA}{V_2}\right)^2$$

For n charges obviously it follows

$$M_{n2} = M_{02}\left(1 - \frac{VDA}{V_2}\right)^n + \sum_{i=0}^{n-1} c_{i1} \cdot VDA\left(1 - \frac{VDA}{V_2}\right)^{n-i} \tag{13}$$

Using equation (5) c_{i1} can be replaced and we get

$$\boxed{M_{n2} = M_{02}\left(1 - \frac{VDA}{V_2}\right)^n + c_{01} \cdot VDA \cdot \sum_{i=0}^{n-1} \left(1 - \frac{VDA}{V_1}\right)^i \cdot \left(1 - \frac{VDA}{V_2}\right)^{n-i}} \tag{14}$$

(14) easily can be applied using Electronic Data Processing, but for the case being at hand only hand-calculators were available. So simplifications had to be introduced. If $V_1 = V_2$ from (14) follows

$$M_{n2} = (M_{02} + n \cdot c_{01} \cdot VDA)\left(1 - \frac{VDA}{V}\right)^n \tag{15}$$

It seems reasonable, in cases of $V_1 \neq V_2$ to introduce the average value $\overline{V} = (V_1 + V_2)/2$ thus giving

$$\boxed{M_{n2} = M_{02}\left(1 - \frac{VDA}{V_2}\right)^n + n \cdot c_{01} \cdot VDA\left(1 - \frac{2 \cdot VDA}{V_1 + V_2}\right)^n} \tag{16}$$

The mistake of this approximation of course will become as bigger as more V_1 and V_2 differ from each other.

For the calculation of ion-exchange plant data the stuff-mass dragged into flow-rinsing bath 3 is of interest. It follows from the mass balance

$$M_{n3} = M_{n1 \rightarrow 2} - M_{n2}$$

giving

$$\boxed{\begin{aligned} M_{n3} = {} & c_{01} \cdot V_1 \left[1 - \left(1 - \frac{VDA}{V_1}\right)^n\right] - M_{02}\left(1 - \frac{VDA}{V_2}\right)^n \\ & - c_{01} \cdot VDA \sum_{i=0}^{n-1} \left(1 - \frac{VDA}{V_1}\right)^i \cdot \left(1 - \frac{VDA}{V_2}\right)^{n-i} \end{aligned}} \tag{17}$$

or simplified

$$\boxed{\begin{aligned} M_{n3} = {} & c_{01} \cdot V_1 \left[1 - \left(1 - \frac{VDA}{V_1}\right)^n\right] \\ & - M_{02}\left(1 - \frac{VDA}{V_2}\right)^n - n \cdot c_{01} \cdot VDA\left(1 - \frac{2 \cdot VDA}{V_1 + V_2}\right)^n \end{aligned}} \tag{18}$$

Calculation formula

Additional prior condition: Stuff recycling from bath 2 to bath 1.

Combination: Water + stuff drag-in/Water + stuff drag-out

In a few cases recycling of a certain share of bath volume 2 (stand-rinsing water plus dragged-in stuff) to bath 1 (process electrolyte/solution) had to be included in the calculations. As exact formula could not be utulized by hand-calculators only quick approximate estimations were carried out.

Within the service life of bath 2 the volume share VR is recycled r-times. The resting stuff-mass prior to the first recycling is M_{n2}/r; M_{n2} was calculated earlier by (16); the number of charges is $m = n/r$. After the first recycling the resting stuff-mass is

$$M_{m2} = \frac{M_{n2}}{r} \left(1 - \frac{VR}{V_2}\right)$$

Prior to the second recycling on the average further M_{n2}/r have been dragged-in, and after the second recycling it remains

$$M_{2m\,2} = \frac{M_{n2}}{r} \left(1 - \frac{VR}{V_2}\right)^2 + \frac{M_{n2}}{r} \left(1 - \frac{VR}{V_2}\right)$$

After r recyclings ($r.m = n$ charges) the resting stuff-mass is

$$M_{rm\,2} = \frac{M_{n2}}{r} \sum_{i=1}^{r} \left(1 - \frac{VR}{V_2}\right)^i$$

$$= \frac{M_{n2}}{r} \left(1 - \frac{VR}{V_2}\right) \sum_{i=0}^{r-1} \left(1 - \frac{VR}{V_2}\right)^i$$

The sum-term represents a geometric series which can be replaced as follows

$$(19) \qquad \boxed{M_{rm\,2} = \frac{M_{n2}}{r} \left(1 - \frac{VR}{V_2}\right) \cdot \frac{\left(1 - \frac{VR}{V_2}\right)^r - 1}{\left(1 - \frac{VR}{V_2}\right) - 1}}$$

The stuff-mass recycled to bath 1 may be etimated by

$$(20) \qquad \boxed{M_{rm\,2 \to 1} = M_{n2} - M_{rm\,2}}$$

The stuff-mass $M_{n\,1 \to 2}$ dragged-out from bath 1 to bath 2 and earlier calculated by (7) now can be adjusted by

$$(21) \qquad \boxed{M_{rm\,1 \to 2} = M_{n\,1 \to 2} - M_{rm\,2 \to 1}}$$

The stuff-mass dragged out from bath 2 into bath 3 is assumed to be proportional to the reduction of M_{n2} to $M_{rm\,2}$:

$$M_{rm\,3} = M_{n3} \cdot \frac{M_{rm\,2}}{M_{n2}}$$

$$(22) \qquad \boxed{M_{rm\,3} = M_{n3} \cdot \frac{(1 - \frac{VR}{V_2})}{r} \cdot \frac{(1 - \frac{VR}{V_2})^r - 1}{(1 - \frac{VR}{V_2}) - 1}}$$

A more exact but time spending way of calculating the recycling formula is possible by using the following equations instead of formula (19), (20), (21) and (22); their application should be considered in future cases.

By reason of simplification it is supposed that the stuff-mass dragged-in from bath 1 into bath 2 can be calculated as $M_{n\,1 \rightarrow 2}$ by equation (7), although in praxis $M_{n\,1 \rightarrow 2}$ is slightly greater because of the r-times recycled stuff thus each time increasing the concentration in bath 1 ($c_{rm\,1}$). Under this condition the mass-balance after r recyclings is

$$(23) \qquad \boxed{M_{n\,1 \rightarrow 2} - M_{rm\,2 \rightarrow 1} = M_{rm\,2} + M_{rm\,3}}$$

The stuff-mass recycled from bath 2 to bath 1 can be acchieved as follows:

After 1st rocycling: $M_{m\,2 \rightarrow 1} = \frac{M_{n2}}{r} \cdot \frac{VR}{V_2}$

After 2nd recycling: $M_{2m\,2 \rightarrow 1} = \left[\frac{2M_{n2}}{r} - \frac{M_{n2}}{r} \cdot \frac{VR}{V_2}\right] \frac{VR}{V_2}$

After 3rd recycling: $M_{3m\,2 \rightarrow 1} = \left[\frac{3M_{n2}}{r} - \frac{2M_{n2}}{r} \cdot \frac{VR}{V_2} - \frac{M_{n2}}{3}\left(\frac{VR}{V_2}\right)^2\right] \frac{VR}{V_2}$

$$= \frac{3M_{n2}}{r}\left(\frac{VR}{V_2}\right) - \frac{2M_{n2}}{r}\left(\frac{VR}{V_2}\right)^2 - \frac{M_{n2}}{r}\left(\frac{VR}{V_2}\right)^3$$

After r recyclings:

$$(24) \qquad \boxed{M_{rm\,2 \rightarrow 1} = M_{n2}\left(\frac{VR}{V_2}\right) - \frac{M_{n2}}{r} \sum_{i=1}^{r-1} (r - i)\left(\frac{VR}{V_2}\right)^{i+1}}$$

For the calculation of the stuff-mass resting in bath 2 and bath 3 the following ratios are assumed as meeting the praxis situation satisfactorily:

$$M_{n2}/(M_{n2} + M_{n3}) = M_{rm\,2}/(M_{rm\,2} + M_{rm\,3})$$

$$M_{n3}/(M_{n2} + M_{n3}) = M_{rm\,3}/(M_{rm\,2} + M_{rm\,3})$$

From those ratios can be deducted

$$(25)\qquad \boxed{M_{rm\,2} = M_{n2}\left(1 - \frac{M_{rm\,2 \rightarrow 1}}{M_{n\,1 \rightarrow 2}}\right)}$$

$$(26)\qquad \boxed{M_{rm\,3} = M_{n3}\left(1 - \frac{M_{rm\,2 \rightarrow 1}}{M_{n\,1 \rightarrow 2}}\right)}$$

M_{n2} and M_{n3} follow from equations (16) and (18), $M_{n\,1 \rightarrow 2}$ from (7) and $M_{rm\,2 \rightarrow 1}$ from (24).

MATHEMATICAL FORMULA

used for calculation of metal-content increase or decrease in metal-electrolytes.

A. Introduction

Variation of metal-concentration in metal-electrolytes is due to different anode and cathode efficiency.

B. Abbreviations

E_{Me} = metal equvalent at 100 % efficiency in g . 1A . 1h
i = flowing current in A
I = current density in A/dm^2
A = cathode or anode surface area in dm^2
t = time in h
η = anode or cathode efficiency in %/100
M_{Me} = Metal deposited in g

The further index A or C means Anode or Cathode.

C. Calculation formula

$$\boxed{\begin{array}{ll} (27) & M_{MeA} = E_{Me} \cdot i \cdot t \cdot \eta_A \\ (28) & M_{MeC} = E_{Me} \cdot i \cdot t \cdot \eta_C \\ \hline (29) & \Delta M_{Me} = E_{Me} \cdot i \cdot t \cdot (\eta_A - \eta_C) \end{array}}$$

If $\Delta M_{Me} > 0$, the metal-concentration increases.
If $\Delta M_{Me} < 0$, the metal-concentration decreases.

The current i can be calculated by $i = \frac{I}{A}$.

COMPREHENSIVE WASTE WATER DATA-LIST

PLATING SHOP: DONG-BO, Bu-Chan near Seoul

	Plant	Waste Water Halfconcentrates Concentrates					Flowing Water		Annual Chemical/Product Load of Waste Water																																			
			Depoisoning																																									
		Neutralization	Cyanide	Chromium (hexavalent)	Others	Other Disposal	Non-cyanide	Cyanide	UR-28T	C-4000	E-1000	# 600	UR-28A	Mp-1	Mp-8	MS-1	AT-64	HCl 33%	HNO_3 65%	H_2SO_4 96 %	NaOH	NH_4OH 25%	No. 200	$ZnCl_2$	NH_4Cl	CuCN	NaCN	Cu-Pyrophosphate	K-Pyrophosphate	$CuSO_4 \cdot 5H_2O$	$NiSO_4 \cdot 6H_2O$	$NiCl_2 \cdot 6H_2O$	H_3BO_3	Na-Citrate	Na-Hypophosphate/ -orthophosphate	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		m^3/a							kg/a																																			
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37		39	40	41	42	43	44	45
	Double-Ni/Cr on Steel or Copper-alloy	26		31	16 Degreasing		750			155 172										3896 1 605	49 69										306 221	49 36	44 32						32 116					
	Zinc (alk.) on Steel	59		39	11 Degreasing		1800	600			659 542	24 54	178 420					1179 1872	495 495 186		295 59																				1769 331	884 166		
	Zinc (acid) on Steel (barrel)	207		384	3 Degreasing		2160		134 134									1480	2238 2355 363					1390	3120		633														8411 440	4206 220	520	284
	Nickel on Steel (barrel)	66			3 Degreasing		1650	600	134 370											8660 1960						198	264				155 659	55 235	22 94											
	Total	358	-	514	33	-	6360	1200																																				
									504 268	172 155	542 659	54	420 178					1872	549	2565	59 69 49			1390	3120	198	897				880	271	126						148		771	386	520	284
																			2850	1																					10180	5090		
												24						2659	2733	12556											461	104	66											

ANNEX 4

COMPREHENSIVE WASTE WATER DATA-LIST

TOTAL COMPLEX OF SEVEN PLATING SHOPS

Pos.	Plating Shops	Waste Water Halfconcentrates Concentrates: Neutralisation	Depoisoning: Cyanide	Depoisoning: Chromium (hexavalent)	Others	Other Disposal	Flowing Water: Non-cyanide	Flowing Water: Cyanide
		m³/a						
1	2	3	4	5	6	7	8	9
1	BONG-SO	315	50	96	56 Degreasing 10 K-Thiocyanate		3510	1330
2	SAM-SHIN	1147	37	122	14 Degreasing 5 Pd-Activation 15 Electroless Nickel		8775 1200 Deionised Water	660
3	SHIN-SHIN	1090	13	76	50 Degreasing 5 Pd-Activation 15 Electroless Nickel 10 K-Thiocyanate		10785 1200 Deionised Water	660
4	BONG-WON	1080	13	76	50 Degreasing 5 Pd-Activation 15 Electroless Nickel 10 K-Thiocyanate		10785 1200 Deionised Water	660
5	JONG-SO	365		514	33 Degreasing		6510	600
6	JUNG-ANG	358		514	33 Degreasing		6360	1200
7	JEONG-IL	1050	17	51	7 Degreasing 5 Pd-Activation 15 Electroless Nickel		10785 1200 Deionised Water	1410
8	TOTAL COMPLEX	5415	130	1449	353	--	52310	6510
9								
10							53510 Deion.Water	
11								
12						Degreasing 243		
13						Pd-Activation 20		
14						Electroless Ni 60		
15						K-Thiocyanate 30		
16								
17								
18								

Annual Chemical/Product Load of Waste Water

Pos.	US-287	C-4000	H-1000	## 600	US-284	Np-1	Np-8	HS-1	AT-64	HCl 33%	HNO_3 65%	H_2SO_4 96 %	NaOH	NH_4OH 25%	No. 200	$ZnCl_2$	NH_4Cl	CuCN
	kg/a																	
1	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
9													154		968			1491
10	1008	824	1054	108	993	1136	8520	2	834	30184	1098	80481	343	141		2783	6433	
11												18412						
12	536	734	1318		2651	230							144		1372			
13							1832			2220								
14														296				
15																57	87	
16									3228		5700	6403						
17				24						2659	2733	8315	8					232
18				78				16		5928	5466	38606		45				

Pos.	NaCN	Cu-Pyrophosphate	K-Pyrophosphate	$CuSO_4 \cdot 5H_2O$	$NiSO_4 \cdot 6H_2O$	$NiCl_2 \cdot 6H_2O$	H_3BO_3	Na-Citrate	Na-Hypophosphite -orthophosphite	KSCN	Acet[illegible]	Brass-sa[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	kg/a																	
1	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
9	4859									144	434	440						559
10		376	1368	8700	9168	1793	1128	2840	1160	8	8		6060	19816	1342	272	1044	
11														20960				
12																		
13																		
14					720			552	220									
15					261		261			42	42							
16													7066	7697	20180	10180		
17	853				1645	307	107			32	66	156						
18		4452	16136	11507	3482	5706	4658											

Only to be filled in if total annual chemical/product consumption is needed for cost calculation, cost distribution and so on.

ANNEX 5

VISIT-REPORT

Date of Visit: 6th of May, 1985

Companies visited:

1. Ban Weol Electroplating Industry Corp.
   60-5 Pal Gok-Lt., Ban Weol-Myon
   Hwa Seong-Kun, Kyung-Ki-Do
   Tel. (0345) 80-0625
2. Kyung-In Electroplating Corp.
   Ban Weol-Myon, Hwa Seong-Kun
   Kyung-Ki Do
   Tel. (0345) 6-6805

Persons met:
At 1.: Mr. Choi, Soon-Syub (Plant Manager)
At 2.: Mr. Oh, Hyun-Tae (Plant Manager)

Accompanied by: Mr. Ro, Hyong-Bo, KIMM

General impression

The companies visited treat the waste water of industrial complexes of up to 40 plating shops. Unfortunately some of these plating shops themselves could not be visited in order to get a picture about the origin of waste waters and the grade of care of their handling until discharge to the waste water treatment plant.

The waste water plants themselves were in an old and poor condition; the waste water treatment scheme seems to be more complicated than necessary and in some cases adjusted to overcome difficulties caused by improper waste water handling in the electroplating shops.

Furthermore there are not so many admitted discharge values as for instance in the United States, Germany and other European countries as well as in Japan; this eases the treatment substantially. So nickel can be discharged unlimitedly, but especially the need of separation of nickel and nickel-complexes from waste water leads to high requirements to be satisfied by a most proper waste water handling in the plating shops and treatment in the waste water plant.

The laboratory was equipped excellently and in a very pleasing condition. Here not only waste water analysises, but also all controls of the various plating solutions for the plating shops are carried out.

The people met was not prepared to put questions, and problems were said not to exist so that a corresponding discussion could not happen.

Special remarks

The waste water treatment plants have a capacity of 600 m^3/day each; the present rate of use is about 50 %. The waste water is generated in plants of decorative Nickel/Chromium-, Hard-Chromium-, Zinc(acid and alkaline-cyanidic)-, Tin- and Brass-Plating. After treatment it is discharged directly into the Anyang-San nearby.

The average costs per month are for

chemicals	19,000,000 Won	(22,350.- US$)
power	1,000,000 Won	(1,175.- US$)
labour	2,000,000 Won	(2,350.- US$)
sludge-discharge	3,500,000 Won	(4,120.- US$)
general	1,500,000 Won	(1,765.- US$)
Total	27,000,000 Won	(31,760.- US$)
or per m^3 waste water	300 Won	(0.35 US$)

The rate of 3 - 5 % of the annual turnover to be spent for waste water treatment is similar to German figures.

The costs are appositioned to the plating shops on the base of power consumption (15 %) and waste water amount discharged (85 %).

Admitted discharge values are (in bracketts typical practical average values of the plants visited):

pH-value	5.8 - 8.0	(8.0 - 8.5)
Cyanide	1 mg/l	(0.5 mg/l)
Copper	3 mg/l	(1 mg/l)
Zinc	5 mg/l	(0.5 mg/l)
Chromium (total)	2 mg/l	(1 mg/l)
Chromium (hexavalent)	0.5 mg/l	(0.1 mg/l)

The equipment of the waste water treatment plants is of Japanese origin. The introduction of a flow-rinsing circuit combined with an ion-exchange plant thus saving of at least 90 % of the present waste water amount is under discussion. Because of the need of adjustment of rinsing techniques in the plating shops concerned and the corresponding costs necessary to meet the demands of ion-exchange treatment in a first step just one plating shop shall be equipped with a flow-rinsing circuit for test and reference purposes.

The waste water analysis-methods are similar to those in the United States and Europe. Heavy metals are determined by atomemissionspectography (AES) which represents a high standard of analytic accuracy and efficiency.

Heavy-metal-cyano-complexes generated by improper waste water handling in the plating shops are cracked by transfer into the most stable ferrocyano-complexes adding ferrosulphate to the waste water share concerned. This in Germany is not allowed, because the ironcyano-complexes may be decomposed later in contact with other garbage at the place of final deposit and release free cyanide into the groundwaters.

Discussion

During the discussion comments were given to typical waste water treatment schemes used in Germany, techniques of cyanide-depoisoning using hydrogenperoxide or ozone, the harmful influence of sulphate-ions onto canal-concrete and the discharge-conditions which German direct-dischargers (dischargers direct into rivers, not indirect via community sewage plants) have to observe in order to avoid unnecessary discharge dues. The calculation method of these discharge dues shortly was explained.

Dr. L. Winkler

ANNEX 6

Waste Water Treating Technology in Metal Finishing Processes

Special Seminar at Academic Meeting of the Korea Metal Finishing Society
at Taegu, May, 4th, 1985.

ABSTRACTS

After a short survey over the present waters protection legislation situation in the Federal Republic of Germany (FRG) the harmful materials in waste water from metal finishing processes and their limiting values are described. The basic principles of waste water treatment from the chemical point of view include depoisoning cyanide and hexavalent chromium, separation of heavy metals by precipitation as hydroxides or organosulphides and final neutralization to the agreed pH-value-range. Generally applied treatment technologies are the flowing-through- and batch-type techniques, the latter one beeing more and more preferred. Although many well developped recycling techniques are available at present they are preferably used by bigger surface finishing companies which are able to carry the investment costs and where the amount of stuff to be recycled pays them within a reasonable period of two to three years. A series of slides gives a picture about waste water treatment equipment in the FRG. Special disposal problems include the separation of sulfate, the cracking of complexes, especially metal-ammonia-complexes, and avoiding an overstep of existing ammonia/ammonium-limiting values as well as the economic disposal of concentrated electrolytes. The future is expected to bring a heavy reduction of the present limiting values, the additional introduction of limiting annual freight values and the total interdiction of self-disposal of concentrated solutions and electrolytes.

1. Legal situation in the Federal Republic of Germany

The basic law of ruling the use of and disposal into natural waters is the Wasserhaushaltsgesetz WHG (Waters Household Law, Oct., 16th, 1976). It is supported and supplemented by corresponding laws in each of the eleven Lands of the FRG and by the necessary enacting legislation.

Natural waters are all still and flowing waters of every size on and beneath the earth surface (lakes, rivers, groundwaters, the sea within the national borders), but not waters in artificially constructed beds, basins or canals.

The basic principles of the WHG are

- The use of natural waters has to serve the public's welfare and to avoide any evitable prejudice.
- The use of natural waters requires a permission of the authorities con-

cerned.

- The permission of use may fix special administrative and technical conditions.
- Contamination of natural waters or endangering anybody's health, life, property by such a contamination will be punished by imprisonment up to five years or fine; in most cases already the attempt of contamination or endangering is punishable.
- Any offence against enacting rules, permission conditions etc. will be fined up to DM 100,000.--.

The use of natural waters has a very far-reaching meaning and includes any type of action, which may have a detrimental influence, so for instance also transport and storage of harmful products like chemicals by means of vehicles, pipelines, containers and others.

The disposal of sanitary and industrial waste water has to observe minimum requirements which has been or are going to be fixed by the Federal Government for each type of industry; these requirements consider the application of waste water treatment technologies of generally accepted standard and efficiency.

The disposal of treated sanitary and industrial waste water into natural waters is subject to a waste water due which is calculated on the basis of the annual amount of waste water discharged, its contents of mercury, cadmium, sludge, oxidable compounds and ist fish-poisonousness. By given mathematical equations values of waters analysises are transferred into detriment-units, and the due per unit started with DM 12,-- in 1981, amounts at present DM 36,-- and will reach the final value of DM 40,-- in 1986. Basis of this regulation is the federal Abwasserabgabengesetz (Law about dues on disposed waste water, Sept., 13th, 1976).

The legal situation described above is, as already mentioned, restricted on the use of and disposal into natural waters (direct disposal); for the disposal into community canals and sewage plants each community issued own sewage statutes, which of course follow basic general recommendations all over the FRG, but also meet special waste water situations in the communities. Most industrial waste water producers dispose into community sewage plants (indirect disposal); the waste water dues paid by the directly disposing communities are distributed to the indirect disposers by regulations fixed in the statutes. Additionally the indirect disposers can be charged for contaminations disposed which are over the limiting values.

2. Harmful components and properties of metal finishing waste water - Limiting values

As most of the metal finishing companies are indirect disposers, the further paper will deal with the indirect waste water disposal into public sewage plants. The german ATV Abwassertechnische Vereinigung e. V. (Waste Water Technique Association, based on voluntary private or company-membership) in cooperation with VKS Verband Kommunaler Staedtereiningungsbetriebe (Association of Municipal Cleaning Utilities) in 1970 published Recommendations for the disposal of waste water into a public sewage plant; these have been revised recently and published as Arbeitsblatt (Working Sheet) A 115 (January 1983); table 1 below shows as a part of A 115 the recommended limiting values in detail. The Working Sheet has been elaborated honorarily by a group of experienced engineers and scientists following rules of ATV; the latter ones include giving an ear to the technical world. A 115 is the basis of the already mentioned community statutes, whereby in the statutes the limiting values generally are lower than in A 115.

3. Basic principles of waste water treatment

On the chemical side the treatment of metal finishing waste water has to include

- depoisoning of cyanide and hexavalent chromium;
- cracking of metal-complexes;
- separation of metals as metalhydroxides or in form of other highly insoluble metalcompounds;
- separation of sludge;
- adjusting of the pH-value to the admitted range.

Using the suitable chemical reactions and treatment-chemicals a special treatment step for separating organic compounds is not necessary; where so not, emulsion-cracking and fat/oil-adsorption by products on silica-basis have to be applied.

The temperature of waste water is almost below 35 °C so that a special cooling is not needed. Except cyanide the authorities concerned do not strongly control anions like sulfate, nitrite or fluoride; where they do, special additional treatment steps have to be applied whenever possible. In the Land Baden-Wuerttemberg there exists a limiting value for ammonia/ammonium, although a reasonable and economic technique for the separation of this stuff does not exist. This special disposal problem will be discussed later.

TABLE 1: Limiting values of treated waste water to be observed before discharge into a community sewage plant

Waste water properties		ATV-Recommendation A 115	Typical Values of Statutes	Minimum Requirements by WHG
General properties				
Temperature	°C	35	35	
pH-value		6,5 - 10,0	6,5 - 9,0	
Sludge removable (after 0,5 h depositing time)	ml/l	10	1,0	0,3
Organic compounds				
Oil/fat (hydrolizable)	mg/l	250	100	
Carbonhydrogen-Compounds	mg/l	20	20 (petrolextractable)	10
Chlorinated solvents (as chlorine)	mg/l	5		
Phenols	mg/l	100	100	
Anorganic compounds				
Arsen As	mg/l	1	0,1	-
Lead Pb	mg/l	2	2,0	1
Cadmium Cd	mg/l	0,5	0,1	0,5
Chromium(VI) Cr	mg/l	0,5	0,2 - 0,5	0,5
Chromium total Cr	mg/l	3	3	2
Copper Cu	mg/l	2	1	2
Nickel Ni	mg/l	3	3	3
Mercury Hg	mg/l	0,05	0,05	-
Selenum Se	mg/l	1		-
Zink Zn	mg/l	5	5	5
Tin Sn	mg/l	5	3	-
Aluminium Al	mg/l	no limit, if not harmful to sewage plant	20	3
Iron Fe	mg/l		10	3
Ammonia/ammonium NH_3/NH_4	mg/l	200	50	100
Cyanide (by chlorine oxidable) CN	mg/l	1	0,2	0,2
Cyanide total CN	mg/l	20	1,0	-
Fluoride F	mg/l	60	10 - 20	50
Nitrite NO_2	mg/l	20		-
Sulfate SO_4	mg/l	600	400 - 600	-
Sulphide S	mg/l	2	-	-
Chlorine Cl_2	mg/l	-	0,5	0,5
Oxidable compounds (Chemical demand of oxygen CSB)	mg/l	in sewage plants must not occur anaerobe conditions	600	600

The chemical oxygen demand CSB (chemischer Sauerstoffbedarf) is regarded as limiting value for the calculation of sewage dues; when exceeded the dues arise, but no punishment or fines threaten. A general and economic way of reducing CSB does not exist; in most cases CSB-values of metal finishing waste water are below the limiting values.

The five basic tasks of waste water treatment mentioned above lead to the general treatment scheme as shown on the next page.

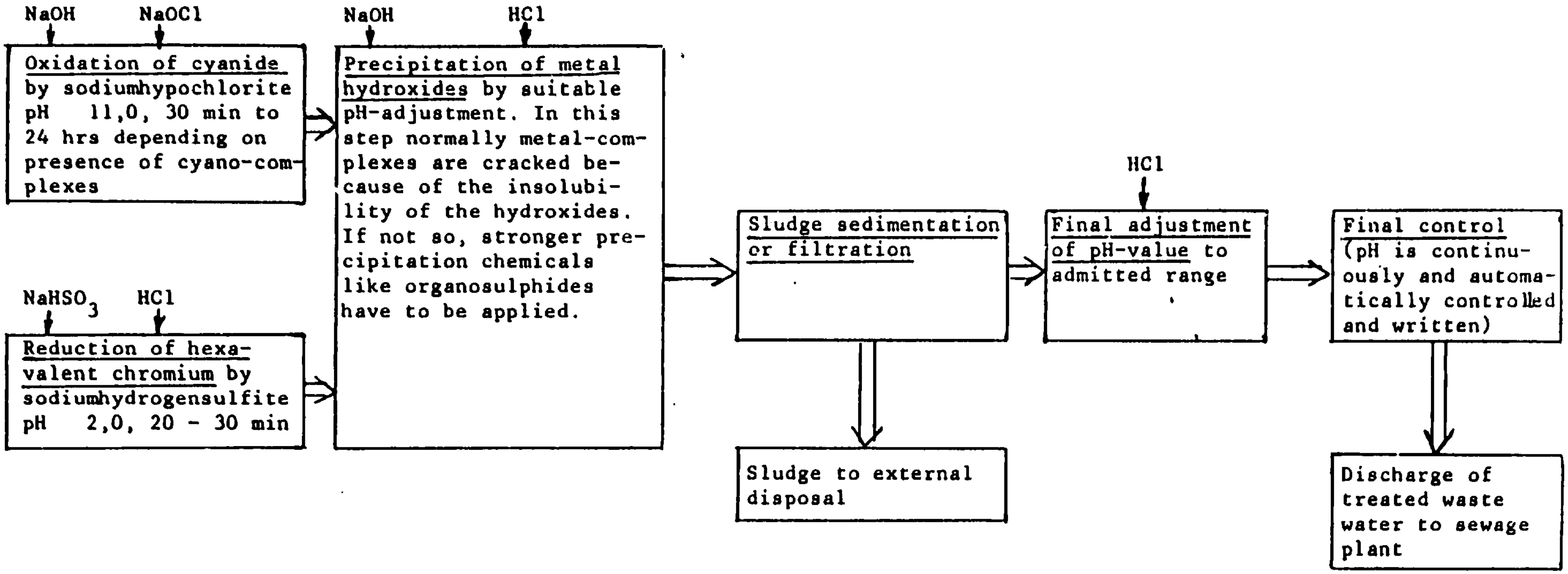
On the technical side waste water can be treated while continuously flowing through the plant or batch-wise. The flowing-through-technique although cheaper in investment has several main disadvantages:

- Inproper treatment, not quickly enough detected, leads to a disposal of waste water with exceeded limiting values.
- Flowing-through-treatment gives the best results when the amount and composition of the waste water stay constant in a narrow range; greater changes caused by varying production rates and changes to new finishing chemicals lead to treatment problems especially when these changes are not readily observed.
- In very diluted waste water chemical reactions do not constantly produce the results necessary for a reliable water quality below the limiting values.
- Generally the flowing-through-technique in Germany is pushed back by the authorities concerned in favour of the batch-type technique.

The batch-type technique forces to reduce the amount of waste water, otherwise the number and/or size of batches would become unefficiently great. So batch-treatment plants are usually connected with a flow-rinsing circuit including an ion-exchange plant for continuous deionizing the flowrinsing water. Such a circuit reduces the waste water amount at least by 90 %. The remaining 10 or lees % now can be batch-treated under economic conditions. The despite higher investment costs widely accepted advantages of the batch-tretament technique are

- The danger of disposing waste water with exceeded limiting values is reduced to nearly nil. Each batch will be discharged into the community sewage system after the final controls have prooved proper treatment.
- Variations in amount and composition of waste water can be met easily.
- Chemical reactions occur more reliably although in concentrated solutions the influences of neurral salts have to be observed.
- The higher investment costs are easily paid within two to three years by saving water supply costs and sewage dues.

Scheme of metal finishing waste water treatment



4. Waste water treatment plants

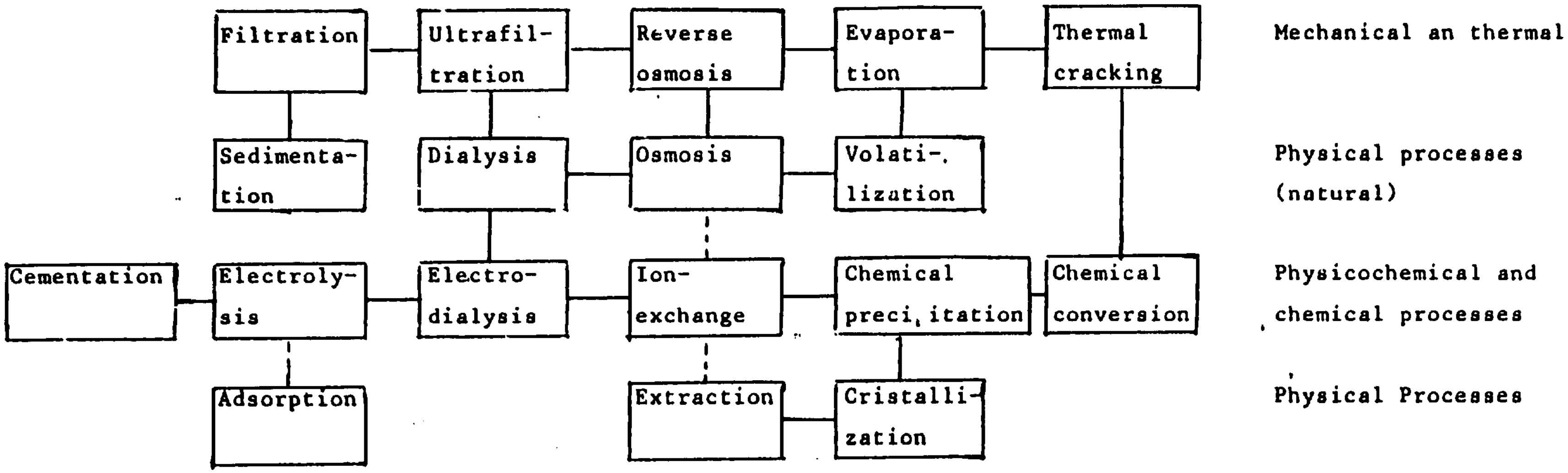
The following slides show typical waste water treatment arrangements in the metal finishing industry:

- small batch-treatment plant;
- great batch-treatment plant;
- automatic batch-treatemnet plant;
- Ion-exchange plant for flow-rinsing circuit;
- Ion-exchange plant with a capacity of 70 m^3/h;
- Ion-exchange plant with 300 m^3/h capacity; the controlling and steering device is installed beneath the floor;
- automatic Ion-exchange plant;
- controlling device with flow-chart of a complete waste water treatment plant including an ion-exchange equipment;
- sludge deposition (flow-treatment 9 m^3/h);
- sludge deposition (new construction of smaller size for flow-treatment 10 m^3/h);
- filterpress and container for sludge collection and transport.

5. Recycling techniques

Waste water treatment does not only start at the waste water treatment plant but already with the production facilities. To avoid waste water is the safest and most economic treatment technique. Apart from the highly controlled use of water and metal finishing chemicals recycling water and material is another way of reducing the generation of wast water and treatment expenses. Although there is a great variety of partly well developped recycling processes apart from the already mentioned flow-rinsing ion-exchange circuit applications are low due to the high investment costs which in moct cases cannot be amortized within an acceptable time of two to three years. Only with bigger surface finishing companies it is worth to install suitable recycling equipment, and there is indeed a greater acceptance for such techniques. However, recycling techniques should not be introduced before other less costly waste water avoiding actions have been successfully realized. So for instance the second step would be done before the first when reversed osmosis is introduced for prolonging service life of degreasing electrolytes without having checked and applied before the best longlasting type of degreasing product and its lowest possible application concentration.

Recycling processes and their interrelation (Metal finishing industry)



(Courtesy: Dr. Goetlemann KG
Stuttgart, FR Germany)

Recycling techniques in Germany well accepted are:

- Rinsing with recycling the recovering rinsing bath;
- Ion-exchange for recovering precious metals like silver and gold;
- Ion-exchange for prolonging service life of chromium-electrolytes in combination with an evaporation and complete recycling of the recovery rinsing bath;
- Acid retardation for prolonging service life of anodizing electrolytes by separation of the salts formed during production. The retardation principle also can be applied on other acid solutions.
- Cristallization.

Especially acid retardation will play a major role in the surface finishing industry in the future.

6 Special disposal problems

Nearly every finishing shop faces special waste water treatment problems the most usual of which are

- Exceeding the limiting values of sulfate (400 or 600 mg/l);
- Ammonia-complex formation and related difficulties in metalhydroxide precipitation and separation (f. i. waste water from electroless nickel-plating solutions, electroless copper-plating electrolytes, solutions of vibration- or barrel-grinding and -polishing).
- Impossibility of ammonium/ammonia separation from waste water;
- Disposal of concentrated electrolytes, especially acids (etching, pickling and polishing solutions).

Sulfate is not harmful to environment but destroys especially in acid solutions the concret of canal-tubes. In order to stay within the limiting values it is advisable to concentrate all sulfate-containing waste water into a special treatment line applying calciumhydroxide or -chloride as precipitation agent; because of the solubility of calciumsulfate about 1600 - 2000 mg/l sulfate remain dissolved, but after filtering-off the calciumsulfate and combining the filtrate with the main part of waste water in most cases the sulfate concentration drops below the limiting value. If this technique cannot be applied because of an too low amount of dilution water, sulfate also can be precipitated by bariumchloride, the price of which howevver is high and the proces has to be controlled carefully by analysises; there has also to be observed a limiting value for barium (10 mg/l).

The difficulty of ammonia-complex formation can be overcome by metalhydroxide precipitation at pH 12 and filtering-off the sludge formed; the filtrate then is adjusted to the limited pH-range 6,5 - 9,0; another technique uses strong precipitation agents like organic sulphides, which however must not be applied in excess, because they are highly fish-toxic.

In the case of ammonium/ammonia itself distilling-off from the waste water under reduced pressure might be considered, but apart from the high working expenses the distilled ammonia has to be adsorbed in a suitable washing solution, and the discharging problem arises again.

A more and more widely accepted solution of the problems touched above is the external disposal of such critical waste water shares by facilities which are owned and run at least partly by Land-authorities. The waste water shares concerned will be collected in the finishing shop and from time to time sent to such facilities by truck or tank-lorry. The costs of this type of disposal, which is strongly controlled by the not yet mentioned german federal Abfallbeseitigungsgesetz (Waste Disposal Law) are in the range of 100,- to 500,- DM/m^3, in many cases however lower than those of self-disposing, if the latter is possible at all. Especially in the case of concentrated acids, which normally easily can be discharged by neutralization consuming an equalent amount of sodiumhydroxide solution chemical costs are at least twice higher than those of an external disposal.

In this connection the attention should be drawn to the waste-exchange system organized by the german Chambers of Industry and Commerce and now slowly being joined by neighbouring European countries. Every month a list of waste offers and demands is published and costfree sent to interested companies. So the author himself could arrange that for instance iron-containing concentrated hydrochloric acid of an electroless nickel-plating shop now regularily is sent to a zinc-galvanizing shop which uses it as pickling acid. The disposer just pays the transport costs (that is roughly one third of the self-disposing costs) and the galvanizer gets a costfree chemical, even of reduced service life.

7. Future outlooks

Main future developments in the waste water treatment field in the FR Germany will include

- a heavy reduction of limiting values to about a tenth of the existing figures;
- the introduction of annual limiting freight values (freight = concentration multiplied by the annual waste water amount) in addition to the existing

limiting concentration values;

- the total interdiction of self-disposal of concentrated solutions (not rinsing solutions) which then have to be sent to the already mentioned external disposal facilities.

The reduction of limiting values will widely promote the application of recycling techniques. The introduction of limiting freight values in addition to the existing concentration values limits the amount of waste water which annually can be discharged. Furthermore the trade with freight values is going to be discussed; a company with good waste water treatment and free annual freight-shares may sell them to another company which needs additional freight in order to overcome treatment problems or being enabled to install new production facilities in the area of limited freights. The introduction of annual freight-limits ensures generally, that the discharge of harmful stuff to the community sewage plants does not exceed values which are detrimental to the sewage plant itself and the treated waste water discharged from there into natural waters. <u>The load of environment is under strict control</u>. The total interdiction of self-disposal of concentrated solutions shall reduce the number of existing waste water treatment problems especially in smaller companies and bring an important part of waste discharge under the control of the excellently equipped external disposal facilities and hereby of the Land-authorities.

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Environment Pollution Control in the German Surface Finishing Industry

Paper presented at the Annual Meeting of the Environment Control Engineers of the Chang Won Industrial Complex at 8th, May, 1985 (Chang Won, Town Hall)

Types of environment pollution from a surface finishing shop (electroplatin, pickling, anodizing, lacquering etc.) are

- waste water
- solid and liquid wastes
- air pollution (in many cases causing further soil and natural waters contamination).

1. WASTE WATER

Waste water arises from discharged concentrates, semi-concentrates (stand-rinsing water, water from lacquering cabines, vapour-washing solutions) and eluates out of ion-exchange plants.

The basic steps of waste water treatment are

- oxidation of cyanide and heavy-metal-cyano-complexes
- reduction of hexavalent chromium
- metal precipitation
- pH-adjustment to the admitted range by neutralization.

Two types of treatment techniques can be applied

- the flowing-through-technique
- the batch-technique.

The chemical reactions of waste water treatment are well known and described; it is an absolute condition that people responsible for and dealing with waste water treatment are familiar with those and connected possible problems.

The cyanide-oxidation includes three reaction steps (foil 1). Reaction I is spontaneous and independant on reaction-pH; reaction II, however, prefers alkaline reaction and so depends strongly on pH. In order to acchieve a reasonable reaction speed, at least pH 11 should be maintained. The hydrolisis of cyanate (reaction III) needs a pH of less than 3; under alkaline and neutral conditions it decomposes very slowly. This might cause difficulties as shown later.

Special attention should be drawn to the depoisoning of heavy-metal-cyano-complexes. Whereas copper-, zinc- and cadmium-cyano-complexes easily can be cracked and oxidized under usual oxidation conditions, the very stabel nickel-cyano-complex needs a pH of at least 11, preferably more, a continuous excess of sodiumhypochlorite of 5 - 10 % during reaction and a reaction time up to 16 - 24 hours. In order to avoid this expensive treatment the formation of nickel-cyano-complexes should be prevented already during waste water generation in the surface finishing facilities. The stability of the iron-cyano-complexes depends on their composition and iron-valency. As their decomposition and oxidation is even more difficult than in the case of nickel-cyano-complexes their formation strictly should be avoided. The technique used in the Republic of Korea of separating cyanide by adding iron(II)-sulphate at low pH in Germany is not allowed, because the iron-cyano-complexes formed can be decomposed later in contact with other garbage at the place of final deposit, and free cyanide the will contaminate the groundwaters.

Except sodiumhypochlorite also hydrogenperoxide or ozone can be used for cyanide oxidation. Their application, however, is restricted because of their higher costs and/or equipment expenses. Furthermore in the case of hydrogenperoxide a catalyst, usually iron-metal, has to be used, but this catalyst does not work in any composition of waste water. The advantage of the use of hydrogenperoxide or ozone is based on the fact, that they are reduced just to water, whereas sodiumhypochlorite forms sodiumchloride; this will be of growing future importance because more and more it is realized that also the content of neutral salts like sodiumchloride or - sulphate in the waste water discharged should be kept to a minimum.

The reduction of hexavalent chromium usually is carried out at pH-values below 3,2, using sodiumhydrogensulfite; the optimum pH-range is 2,0 - 2,5, and lower pH-values do not improve the reaction yield. In many cases the hexavalent chromium containing waste water is neutral or alkaline, so that pH 2,0 - 2,5 has to be acchieved by adding hydrochloric acid; this however increases chemical costs and neutral salt concentration in the waste water discharged. In such cases sodiumdithionate should be applied, because it reduces hexavalent chromium quite easily also under neutral or alkaline conditions. At strong alkaline pH-values also ferrosulphate can be used as a cheap reduction chemical.

Difficulties may occur when cyanide oxidation and hexavalent chromium reduction have to be carried out one after another. As already mentioned the cyanide oxidation product cyanate is stabel under neutral and alkaline conditions. If now for chromium(VI)-reduction dithionate is applied cyanate may be reduced simultaneously to cyanide, and the waste water discharged contains cyanide although the cyanide oxidation was carried out before quite properly. In such cases the hexavalent chromium reduction must be carried out at pH 2,0 - 2,5 using sodiumhydrogensulfite; under those conditions cyanate hydrolizes quickly to ammoniumcarbonate, and gassing shows the evolution of carbondioxide. A reduction of cyanate to cyanide cannot longer occur.

The precipitation of metallhydroxides usually is carried out by adjusting the pH-value to the admitted range of 6,0 - 9,5, sometimes 10,0. However, it is difficult to find a suitable pH-range for the simultaneous precipitation of various heavy metals. Especially nickel requires a pH of at least 9,3 for sufficient precipitation below the admitted discharge value of usually 3,0 mg/l, but under such conditions especially precipitated chromiumhydroxide redissolves as chromiumhydroxocomplex. This problem can be overcome by adding calciumions in form of calciumhydroxide or calciumchloride, because the calciumsalt of the chromiumhydroxocomplex is insoluble.

In this connection attention should be drawn to three significant items:

- lowering of pH during sludge-aging connected with a redissolution of precipitated metalhydroxides, preferably nickelhydroxide;
- formation of nickel- and copper-ammoniacomplexes just at and over the optimum nickel precipitation pH-value;
- improving sludge properties by adding calcium-ions during the metal precipitation step.

Foil 1

CYANIDE-OXIDATION:

I. $2 CN^- + 2 OCl^- + 2 H_2O \longrightarrow 2 CNCl + 4 OH^-$

II. $2 CNCl + 4 OH^- \longrightarrow 2 CNO^- + 2 Cl^- + 2 H_2O$

IIIA. $2 CNO^- + 3 OCl^- + H_2O \xrightarrow{Ox.} N_2 + 2 CO_2 + 3 Cl^- + 2 OH^-$

IIIB. Hydrolysis

$$CNO^- + 2H_2O \begin{array}{l} \nearrow NH_4^+ \quad + \quad HCO_3^- \\ \qquad\quad OH^- \updownarrow H^+ \\ \searrow NH_3 \quad + \quad CO_3^{--} \end{array}$$

CYANO-COMPLEXES

$Fe(CN)_6^{4-}$

$Ni(CN)_4^{2-}$

$Cu(CN)_4^{3-}$

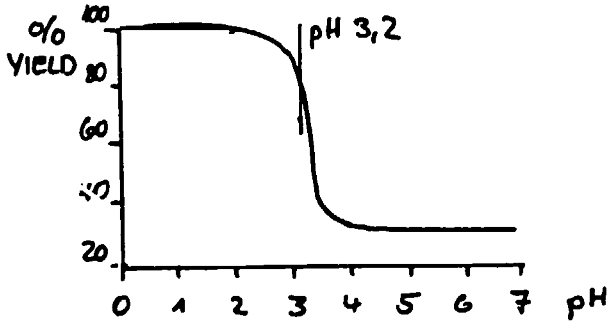
$Zn(CN)_4^{2-}$

$Cd(CN)_4^{2-}$

↑ STABILITY-INCREASE

CHROM(VI)-REDUCTION

$$Cr_2O_7^{--} + 3 HSO_3^- + 8 H^+ \longleftrightarrow 2 Cr^{3+} + 3 HSO_4^- + 4 H_2O$$



$NaHSO_3$: < pH 3,2

$Na_2S_2O_4$: pH 2-12

$FeSO_4$: > pH 11

As a result of the metal precipitation problems shortly touched above it is more and more preferred to separate metal precipitation and pH-adjustment into two following steps. The metal precipitation is carried out at the most optimum pH-value without any regard to the admitted pH-range. The final pH-adjustment follows after having filtered-off the precipitated hydroxide-sludge.

The four steps of waste water treatment mentioned before lead to the most effective general treatment scheme shown on page 4 (foil 2). On the technical side waste water can be treated while continuously flowing through the plant or batch-wise. The flowing-through-technique although cheaper in investment has several main disadvantages:

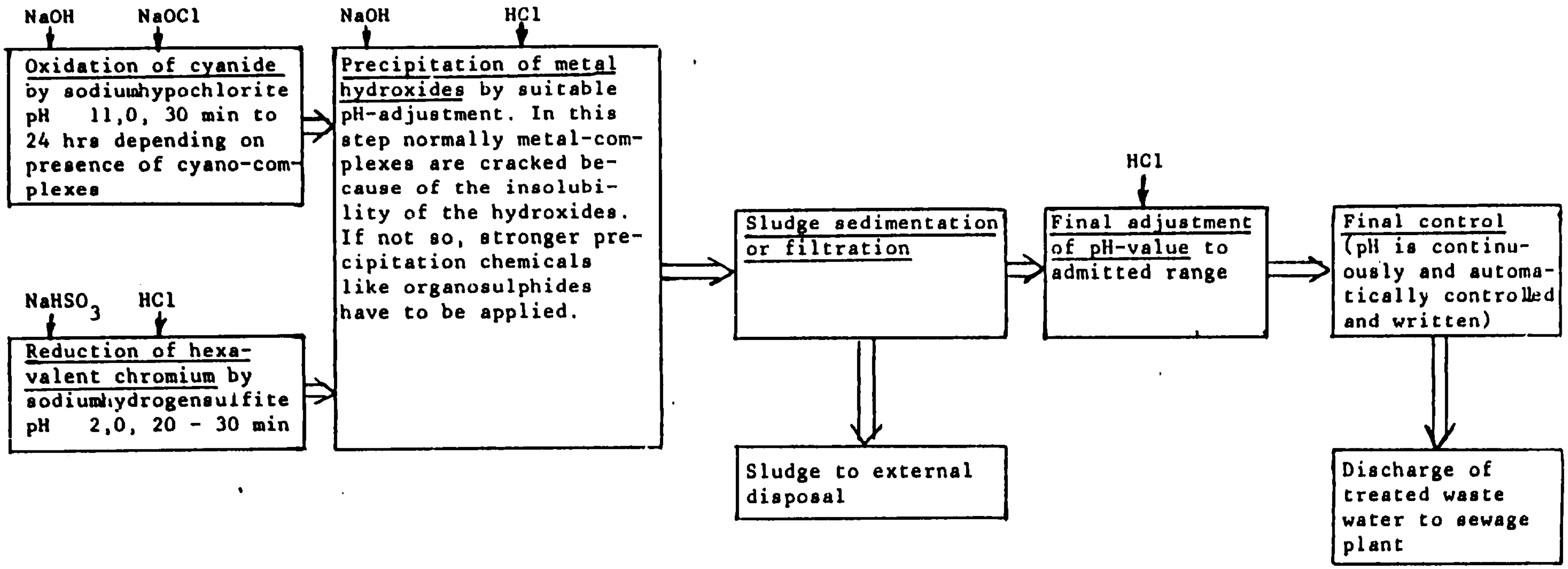
- Inproper treatment, not quickly enough detected, leads to a disposal of waste water with exceeded admitted values.
- Flowing through-treatment gives the best results when the ammount and composition of the waste water stay constant in a narrow range; greater changes caused by varying production rates and changes to new finishing chemicals lead to treatment problems especially when these changes are not readily observed.
- In very diluted waste water chemical reactions do not constantly produce the results necessary for a reliable water quality below the admitted values.
- Generally the flowing-through-technique in Germany is pushed back by the authorities concerned in favour of the batch-type technique.

The batch-type technique forces to reduce the amount of waste water, otherwise the number and/or size of batches would become unefficiently great. So batch-treatment plants are usually connected with a flow-rinsing circuit including an ion-exchange plant for continuous deionizing theflowrinsing water. Such a circuit reduces the waste water amount at least by 90 %. The remaining 10 % or less now can be batch-treated under economic conditions. The despite higher investment costs widely accepted advantages of the batch-treatment technique are

- The danger of discharging waste water with exceeded admitted values is reduced to nearly nil. Each batch will be discharged into the community sewage system after the final controls have proved proper treatment.
- Variations in amount and composition of waste water can be met easily.
- Chemical reactions occur more reliably although in concentrated solutions the influence of neutral salts has to be observed.
- The higher investment costs of batch-treatment plants including an ion-exchange plant are easily paid within two to three years by saving water supply costs and sewage dues.

With regard to harmful components and properties of surface treatment waste water and admitted discharge values the german ATV Abwassertechnische Vereinigung e. V. (Waste Water Technique Association, based on voluntary private or company-membership) in cooperation with VKS Verband Kommunaler Staedtereinigungsbotriebe (Association of Municipal Cleaning Utilities) in 1970 published Recommendations for the discharge of waste water into a public sewage plant; these have been revised recently and published as Arbeitsblatt (Working Sheet) A115 (January 1983); table 1 on page 5 shows as a part of A115 the recommended admitted values in detail. The Working Sheet has been elaborated honorarily by a group of experienced engineers and scientists following rules of ATV; the latter ones include giving an ear to the technical world. A115 is the basis of the community statutes, whereby the

Scheme of metal finishing waste water treatment



Oxidation of cyanide by sodiumhypochlorite pH 11,0, 30 min to 24 hrs depending on presence of cyano-complexes

Reduction of hexavalent chromium by sodiumhydrogensulfite pH 2,0, 20 - 30 min

Precipitation of metal hydroxides by suitable pH-adjustment. In this step normally metal-complexes are cracked because of the insolubility of the hydroxides. If not so, stronger precipitation chemicals like organosulphides have to be applied.

Sludge sedimentation or filtration

Sludge to external disposal

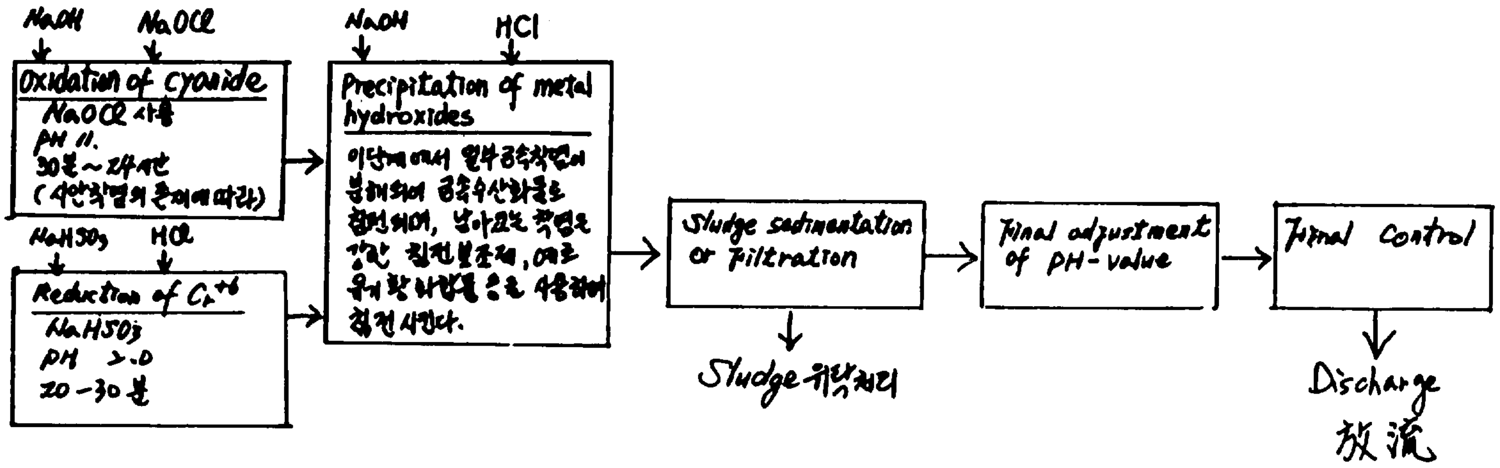
Final adjustment of pH-value to admitted range

Final control (pH is continuously and automatically controlled and written)

Discharge of treated waste water to sewage plant

2

Scheme of metal finishing Waste water treatment.
표면처리공장의 기본 폐수처리 공정.



Foil 2

TABLE 1: Limiting values of treated waste water to be observed before discharge into a community sewage plant

Waste water properties		ATV-Recommendation A 115	Typical Values of Statutes	Minimum Requirements by WHG
General properties				
Temperature	°C	35	35	
pH-value		6,5 - 10,0	6,5 - 9,0	
Sludge removable (after 0,5 h depositing time)	ml/l	10	1,0	0,3
Organic compounds				
Oil/fat (hydrolizable)	mg/l	250	100	
Carbonhydrogen-Compounds	mg/l	20	20 (petrolextractable)	10
Chlorinated solvents (as chlorine)	mg/l	5		
Phenols	mg/l	100	100	
Anorganic compounds				
Arsen As	mg/l	1	0,1	-
Lead Pb	mg/l	2	2	1
Cadmium Cd	mg/l	0,5	0,1	0,5
Chromium(VI) Cr	mg/l	0,5	0,2 - 0,5	0,5
Chromium total Cr	mg/l	3	3	2
Copper Cu	mg/l	2	1	2
Nickel Ni	mg/l	3	3	3
Mercury Hg	mg/l	0,05	0,05	-
Selenum Se	mg/l	1		-
Zink Zn	mg/l	5	5	5
Tin Sn	mg/l	5	3	-
Aluminium Al	mg/l	no limit, if not harmful to sewage plant	20	3
Iron Fe	mg/l		10	3
Ammonia/ammonium NH_3/NH_4	mg/l	200	50	100
Cyanide (by chlorine oxidable) CN	mg/l	1	0,2	0,2
Cyanide total CN	mg/l	20	1,0	-
Fluoride F	mg/l	60	10 - 20	50
Nitrite NO_2	mg/l	20		-
Sulfate SO_4	mg/l	600	400 - 600	-
Sulphide S	mg/l	2	-	-
Chlorine Cl_2	mg/l	-	0,5	0,5
Oxidable compounds (Chemical demand of oxygen CSB)	mg/l	in sewage plants must not occur anaerobe conditions	600	600

in the statutes the admitted values generally are lower than in A115. (The community statutes rule the conditions of and dues for the discharge of treated waste water into community canals and sewage plants).

The analytic control of admitted discharge values is done by usual techniques like atomemissionspectography in the case of metals, infraredspectography and other agreed water control methods following the Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung (German Common Methods for Analysis of Water, Weste Water and Sludge) elaborated and published by the Fachgruppe Wasserchemie (Section Water Chemistry) of the Gesellschaft Deutscher Chemiker (German Chemists' Society). The surface finisher, however, these facilities has not available; he works with hand-set tests which rely on a photometric basis and supply sufficient results for the practical daily work.

2. SOLID AND LIQUID WASTES

Solid and liquid wastes to be discharged from a surface treatment shop are sludge (liquid or solid, the latter with about 60 % water) from waste water treatment plants, aqueous concentrated electrolytes of special composition, which cannot be treated in the existing plant without problems, and organic solvents like flourinated or especially chlorinated carbonhydrogens (FCH or CCH). Such wastes are discharged externally in well equipped utilities; organic solvents generally are redistilled for repeated use. Advantages of an external discharge are less problems with self-discharging and in many cases lower costs. The wastes concerned are collected in the treatment shop and from time to time sent to the mentioned external facilities by trucks, multi-lift vehicles or tank-lorries. The costs of external discharge which is strongly controlled by the german federal Abfallbeseitigungsgesetz (Waste Discharge Law) are in the range of DM 100,- to 500,- per ton (1000 kilogramms), in many cases, however, lower than those of self-discharging, if the latter is possible at all. Especially in the case of concentrated acids, which normally easily can be discharged just by neutralization consuming an equvalent amount of sodiumhydroxide chemical costs for neutralization are at least twice higher than those of external discharge.

In this connection the attention should be drawn to the waste-exchange system organized by the german Chambers of Industry and Commerce and now slowly being joined by neighbouring european countries. Every month a list of waste offers and demands is published and sent costfree to interested companies. The author himself could arrange by this system that for instance iron-containing concentrated hydrochloric acid of an electroless-nickel plating shop now regularily is sent to a zinc-galvanizing shop which uses it as pickling acid. The discharger just pays the transport costs (that is roughly one third of the self-discharging costs) and the galvanizer gets a costfree chemical, even of partly reduced service life.

3. AIR POLLUTION

Air pollution normally is no urgent problem in the surface treatment industry if proper equipment is applied. Sources of air pollution might be electrolyte drops extracted by the exhausting syetem and not or not properly washed out of vapours from hot and/or gassing solutions like chromium- or electroless-nickel-plating solutions, degreasing solutions working at elevated temperatures, pickling and etching electrolytes. Efficient exhausting and washing equipment can reliably avoid any air pollution; only in the case of nitric acid and the various nitrogenoxides evolved from this acid problems exist, because the gas-washing efficiency here is as low as 40 %.

Exhausting- and washing-systems have to be applied separately for both cyanidefree and cyanide containing bathes, otherwise metal-cyano-complexes will be formed which cause, as already discussed, difficulties during the final treatment of the washing solutions in the waste water treatment plant.

A serious problem of combined air- and water-pollution by chlorinated organic solvents was detected recently. The groundwater increasingly is contaminated by this stuff, and the water supply utilities have to apply increasing efforts and costs to purify the water from it. Chlorinated organic solvents in the surface treatment industry are mainly applied in the form of Perchlorethylen, Trichlorethylen and 1,1,1-Trichlorethan. The various origins of this trouble have not yet established surely in all cases of types and industries, but one likely possibility is the exhaustion from solvent-cleaning plants. As the solvents are heavier as water and air, they easily dew down outside of the production buildings and are washed into the soil or the community sewage system by rain. In both cases they finally contaminate the groundwater; to remove it from there by pumping-off is most expensive, because contrary to oil-contaminations it does not swim on the groundwater surface but sinks down to the deepest spots of the groundwater lakes, which prior have to be found by a geological analysis.

4. FUTURE OUTLOOKS

Main future developments in the waste water treatment field in the Federal Republic of Germany will include

- a heavy reduction of admitted discharge values to a tenth of the existing figures;
- the introduction of annual discharge freight values (freight is the product of concentration value and annual waste water amount) in addition to the existing admitted concentration values;
- the total interdiction of self-discharge of concentrated solutions (not rinsing solutions) which then have to be sent to the already mentioned external discharge facilities.

The reduction of discharge values will widely promote the application of recycling techniques. The introduction of admitted discharge freight values in addition to the existing concentration values limits the amount of waste water which annually can be discharged. Furthermore the trade with freight values is going to be discussed; a company with good waste water treatment and free annual freight-shares may sell those to another company which needs additional freight in order to overcome treatment problems or being enabled to install new production facilities in the area of limited freights. The introduction of annual freight-limits ensures generally, that the discharge of harmful stuff to the community sewage plants does not exceed values which are detrimental to the sewage plant itself and the natural waters which the treated waste water is discharged in. The load of environment then will be under strict control!

The total interdiction of self-discharge of concentrated solutions shall reduce the number of existing waste water treatment problems especially in smaller companies and bring an important part of waste discharge under the control of the excellently equipped external discharge facilities.

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환경오염방지기술세미나

(주제 : 서류 표면처리공업의 환경오염관리)

1985. 5. 8.

주최 : 창원기계공업공단

후원 : 한국기계연구소

" 요 약 문 "

표면처리공업, 즉 전기도금, 산세(Acid Pickling), 양극산화, 도장 분야등의 공장에서 배출되는 환경오염 물질은 다음의 3가지로 나눈다.

1. 폐 수
2. 고형 및 액상폐기물
3. 대기오염

이하 이들 3가지 형태의 환경오염에 대해 발표할 내용을 간추려본다.

가. 폐수

폐수는 표면처리 공업에서의 수세수및 도장공장에서의 폐수,증기 세정용액등의 비교적 농도가 높은 폐액과 농도가 진한 폐액 그리고 이온교환수지 공장에서 배출되는 폐수등이 있다.

폐수처리의 기본단계는 극독물로 분류되는 시안이온(및 티오시안이온) 6가크롬등을 무해화시키고, 적합한PH 조절또는 강한 침전제로서 금속을 수산화물로 침전시키며, 착염화물(Complex 화합물)의 분해, Sludge 분리와 마지막으로 법규에 규정된 PH 범위로 중화시켜 방류하게 된다.

이때 폐수처리 기술은 크게 두가지 방법으로 나눌수 있다.

- 연속 폐수처리 (Continuous Systen)
- batch 식 방법(batch Systen)

이중 batch 식 방법은 효과가 높은 방법이며, 많은 장점을 갖고있다.

현재 법규에 규정된 배출 기준값은 폐수처리 반응에 대한 전문적인 지식과 이들 적용조건에 대한 세심한 주의를 요구한다.

차아염소산소다나 과산화수소에 의한 시안이온의 해독 반응과 중아황산소다에 의한 6가크롬의 해독반응은 이미 잘알려져 있다.

금속수산화물의 침전에서는 최적PH 값이 관찰되어져야 하나, 만약 동시에 여러금속이 침전되면 문제가 발생된다.

이때 일반적인 예로 Ca^{tt} 이온이 $Ca(OH)_2$나 $Cacl_2$로서 도움을 줄것이다.

금속착염의 형성은 시안이온(Cyanides), 글루콘산염(gluconates) 폴리인산염(Poly Phosphates), 암모니아,유기아민류(Organo amines) 그리고 특히 EDTA(Ethylene Diamine tetra Acetic Acid), NTA (Nitrile Tetracetic Acid)와 같은 물질에 의해 일어난다.

이밖에 착염을 분해시키는 특수한 기술이 있다.

폐수의 규정 방출값의 분석관리는 금속의 경우 원자흡광법(Atomadsorption Spectro graphy)으로, 그밖에 적외선 분광법 (Infrared Spectro graph) 그리고 기타 수질분석법에 의해서 행해진다.

그러나 표면처리 공장에서는 이러한 설비가 없으며, 측광법(Photometry)에 기초를 두는 Hand - Set tests를 하고있다.

나. 고형 그리고 액상폐기물

위와같은 폐기물은 폐수처리 공장으로부터 또는 폐수처리공장에서 처리될수 없는 특수한 조성을 갖는 수용성,농축물 그리고 탄화수소 화합물에 염소또는 불소가 가미된 유기용매로 부터 나오는 Sludge(약 60% 수분 함유)를 말한다.

이러한 폐기물은 적정설비를 통해 처리되어 외부로 배출되고 유기용매는 일반적으로 재 증류하여 다시 사용한다.

이때 외부 배출의 장점은 자체내 처리보다 문제발생이 적고 비용도 저렴하게 된다.

서독에서의 폐기물 처리법에 의한 외부방출의 엄격한 규제와 이에 대한 폐기물 고환제도가 소개되며, 이때의 경제적인 장점을 예시한다.

다. 대기오염(air Pollu tion)

대기오염은 적절한 장치를 갖춘다면 일반 표면처리 공업에서는 큰 문제가 없다.

대기오염의 원인은 닥트나 후드의 배기 Systen 에 의해 추출된 전해액과 고온에서의 용액기화 등이며,

예로, 무전해 니켈도금의 경우에서이며, 그밖에 고온탈지작업, 산세 Etching 그리고 크롬도금등을 들수있다.

효율적인 배기와 세정장치가 중요하며, 이로써 대기의 문제는 해결된다.

다만 질산의 경우와 질소산화물의 경우는 기체 세정효율이 약 40% 정도이므로 문제가 될수있다.

시안이온이 있거나 시안이온을 함유한 욕조(bath)의 경우 배기 세정 System 이 따로 구분되어 사용하며, 그렇지 않으면 금속시안 착염화합물이 형성되어 나중에 폐수처리 공장에서 세정용액의 마지막 방출과정에 큰 문제를 야기시킨다.

최근에 Trichloro ethylene과 Perchloroethyiene 과 같은 염소화된 유기용매가 대기및 수질오염에 복합적으로 작용하는 문제가 밝혀졌으며, 이들 문제의 해결가능성도 이 세미나를 통해 나타날 것이다.