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CyanoMat® – Modern Cyanide Treatment by UV-Oxidation

Practical Examples from Installations

By Martin Sörensen and Jürgen Weckenmann
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1 The history of UV-oxidation

1.1 The technology of the first and second generation

UV-disinfection was used on a large scale for the first time to treat microbiological organisms in drinking water in Marseille in 1907 is today a well established process for the treatment of potable and process waters. It is increasingly replacing the chlorine treatment.

In the mid 70's UV-oxidation was successfully used to treat the contaminated chlorinated complexes of underground waters. These first technological successes prompted various companies to enter the market with great optimism, concentrated particularly in the treatment of cyanide contaminated waters from the metal finishing industries. Great expectations were awakened. The illusion was that it was enough to put lamps in tubes, cover it up with stainless steel coating and this way the reactor was finished. As a result of these proceedings many unhappy customers were left behind.

Big problems appeared at the time in particular with the siting of the radiation tubes, not enough reaction, corrosion of the reactors and frequent foaming over of the charge container.

The reasons behind this were mostly due to inexperience in the reactor technology, insufficient information available in the processes of peripheral equipment and insufficient understanding of the cyanide treatment processes.

So even today there are plenty of comments, that the treatment of metal cyanides with reactions with OH-radicals has been withdrawn. It is a fact that under conditions in which OH-radicals in the lack of UV-rays there is no effective degradation of cyanide complexes [1, 2].

1.2 The third generation technology

The modern cyanide treatment was developed between 1997 and 1998 by the *a.c.k. aqua concept GmbH* company by treating in a multi stage process. In this way the UV-process is backed by a newly and completely designed reactor and, on the other hand, additional technical process steps that compliment the UV-process.

The cylinder of the UV-reactor is made from borosilicate because of the highly corrosive conditions. The reactor creates an internal rotation of the stream, that together with a chemical backed high turbulence (Re ~10^6) stops the radiation lamps from becoming dirty. A newly developed electronic performance control ensures a constant UV-output, that not only creates a high level chemical reaction, but also more than doubles the life of the lamps, with positive impact on the treatment costs.

The method itself, as a timely development of the process steps, was for the first time in 1999 awarded an environmental achievement and has established itself since then in the galvanotechnical industries. Many modern companies are installing this process.

It incorporates basically a pre-oxidation, where in the pre-treatment a process reaction of water peroxide with free cyanide occurs. This ensures that the over foaming of the containers is kept in control. At this stage the free cyanide and a large part of the cyanide complexes are treated.

The next step is the main oxidation by ***lower pH-value*** under connecting the UV-reactors. In this way the cyanide complexes are destroyed. This reaction step is, for safety reasons, carried out in a separate secure room. In this way it is ensured that in the case of deviations from the normal process, toxic gases are not released. The *sour cyanide treatment* is the innovative core of the *a.c.k.* process and builds together with the security method and the guide technique of *CyanoMat*®. This combination has been registered as a patent. The security technique is built in such a way that no costs for maintenance or chemicals are required.

In the third and final step the elimination of the nitrates-metal complexes and the conditioning before flocculation.

A major advantage is that the majority of the concentrates that are created in the processes, by keeping the running parameters can also be treated. The treatment costs for the chemical for cyanide treatments *CyanoMat*® are, as a rule, considerably less expensive than the classical chloride treatment chemicals.

Against the frequent comments that UV-oxidation does not work in cloudy and highly coloured media, nearly all of the installed *a.c.k.* systems prove the contrary.

In cyanide concentrates of a few mg/L up to 80,000 mg/L there are nearly all types of process waters and stripper concentrates in the surface treatment industries covered, and every installation achieves the agreed performance. The cyanide concentrates after treatments are under the consent limits and the metal consent levels are achieved after the process of: detoxing – flocculation - filtration - final exchange treatment.

Even during the nickel bath conditioning UV-oxidation is successful with persistent organics, although the optical visibility is less than 1 mm [3]. UV-oxidation has also been successfully applied to the treatment of organic complex substances and the elements have been totally destroyed [4]. With help from a special stream guidance *a.c.k*. has also implemented a UV-oxidation system for the treatment of cryogenic PAK using a closed system. [5].

With the *CyanoMat*®-systems, *a.c.k.* has collected experience in Germany and worldwide. As one of the new systems, *CyanoMat*® will be delivered to the company *Otto Seidel Noble Metals Plating* in Karlsruhe. This will be in very close proximity to our own company, and a demonstration facility (*Fig. 1*) for interested companies.

In this way a method is available, that not only ensures that the consent levels for cyanide and metals are achieved, but also to meet the consent levels for AOX.

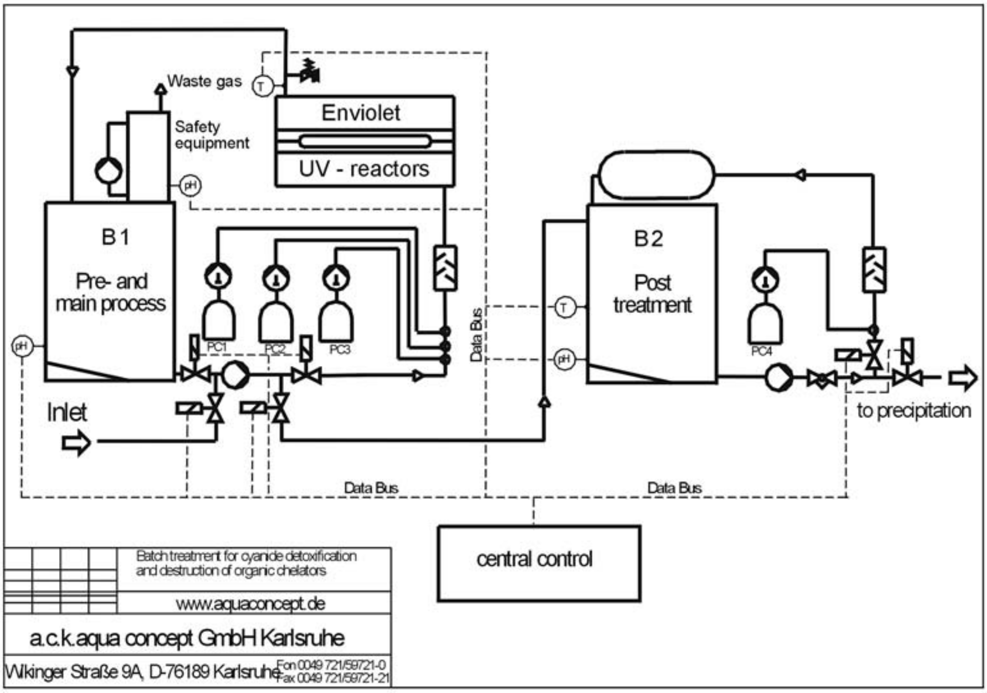

Fig. 1: Scheme of CyanoMat®-process

2 References from the metal finishing industries

A few selected references below, from already close to 100 installed systems in nearly all branches of the metal treatment industry, will give an overview of the breadth of applications. With very few exceptions all waters treated are heavily colored and cloudy. The range of cyanides vary from the lower g/L region up to 80 g/L.

2.1 FUBAG Metal Plating AG (CH)

By Lukas Büchler

The company *FUBAG Metal Plating AG* is a medium size job plater that has for over 80 years been plating metal and plastic surfaces. For the decorations industry very high quality requirements must be met. The department of *light metals plating* uses, amongst other processes, zinc, nickel, silver, gold, etc., mostly as technical surfaces.

In 1998 a complete new de-toxing plant was designed and ordered. Within the scope of the new building for the water treatment plant the future problem of cyanide treatment (chloride lime) was addressed and at the end replaced by a UV-oxidation system.

At this time, this was the first UV-installation for cyanide treatment in Switzerland. The decision for UV was clear, chlorination had always caused major problems (treatment times/handling, hazards/gases) and the new management had for some years pursued all possible modernization of processes and environmentally friendly practices.

Although the installation of the UV-system was well investigated, there were still some quiet concerns in the background, because UV-oxidation did not have a good image in the plating industry.

These concerns have since been totally put aside: *The CyanoMat® treatment (Fig. 2) works reliably and precisely, like a Swiss watch. Since the commissioning there have been no problems with the process waters discharged.* This is the case although all process waters are treated in-house.

We would like to point out the following advantages:

- Negligible faults with the system,
- Minimal service and time requirements,
- Total elimination of chloride lime,

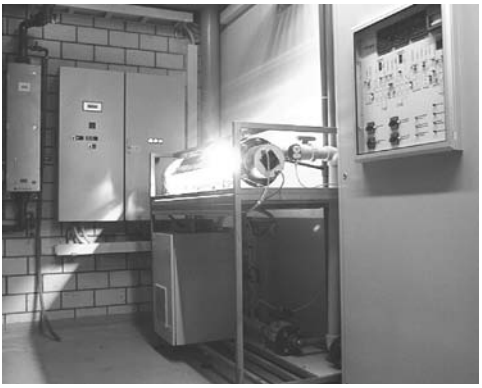

Fig. 2: Enviolet UV-reactor of CyanoMat®-system at FUBAG

- No more corrosion caused by chloride gases,
- Cost effective treatment.

Because of the very short time required for the treatment and long idle times of the UV-installation, this has led to putting the waste waters of chemical nickel as well as the cyanide stripper concentrates through the unit.

The typical figures for the cyanide waste waters are shown on *Table 1*. The water is treated fully and automatically in one batch. Nitrate from metals is also eliminated during the treatments of the cyanide and flocculation of the metals. The consent levels are achieved before the final Ion exchange treatment.

Tab. 1: Effluent data of FUBAG

	Waste water	*After treatment*
Waste water in m^3/d	5	5
Cyanide in mg/L	6.500 – 10.000	< 0,2
Copper in mg/L	approx. 5.000	< 0,3
Nickel in mg/L	10.000 – 15.000	< 0,25
Zinc in mg/L	approx. 1.000	< 0,4
Silver in mg/L	approx. 10	< 0,1
Gold in mg/L	traces	n.d.
Treatment time	4,5 h	
Color	brown-green	clear

2.2 Friedrich Binder GmbH & Co. (D)

Friedrich Binder GmbH & Co (Mönsheim) manufactures gold and silver jewelry chains. During the production process cyanide contaminated process waters are created and are treated in the company's own effluent plant.

To reclaim the precious metals and pre-oxidation of the cyanide content, an electrolysis system is used as pretreatment. The cyanide content after this pre-treatment is around 100 mg/L. In the subsequent treatment, with the classic process of cyanide oxidation with natriumchloride, could the consent limits of weak bound cyanides of 0.2 mg/L after long reaction times with a very high oxidants overdosing, be achieved.

Particularly difficult to treat were batches of increased precious metals by products' content and regenerates of the anion exchanger.

The alternative treatment method with hydrogen peroxide and exposure to ultra violet rays should bring improvements to the present situation. The proper systems from the company *a.c.k.* are used for the treatment of cyanide contaminated water for a few grams per litre, in this way a content of 100 mg/L should pose no problem. Tests were carried out using our samples at the laboratories of *a.c.k.* and treated successfully, however for the small concentration of the effluent an unexpectedly high energy requirement of between 30 and 40 kW h/m^3 was required.

For this we installed a 12 kW *Enviolet* UV-installation (*Fig. 3*). The planned treatment time of 2.5 m^3 was approx 8 hours. In practice with different composition of process waters, it showed that in some cases even longer treatment times which increased during production and the storage of the system. To treat the quantity of contaminated water, a regular cleaning of the treatment system was required. An improvement was retrofitted.

Through a combination of pre-treatment, process steering and additions of some hardware, we could avoid the storage in our system alltogether and also reduce the treatment times quite considerably. Since then the concentration of the weak bound cyanides disposed are, as a rule well, below 0.1 mg/L (*Tab. 2*).

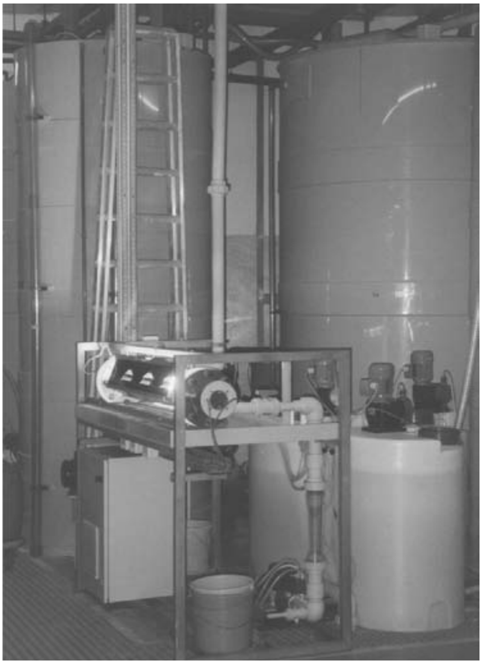

Fig. 3: Enviolet® UV-reactor in CyanoMat®-system at Binder

Tab. 2: Effluent data Friedrich Binder GmbH & Co

	Waste water	*Environmental control 18.07.01*
Waste water in m^3/d	3	3
Cyanide in mg/L	100	0,08
EOX in mg/L	1	0,29
Copper in mg/L	50	< 0,05
Nickel in mg/L	50	< 0,05
Silver in mg/L	15	0,01
Zinc in mg/L	20	0,20
Treatment time	8 - 12 h	
Color	none	none

2.3 Surface treatment in Berlin GmbH & Co (OTB) (D)

By Prof. Dr. Uwe Landau, Ing. Frank Boschan, Dipl.-Chem. Ralph Popp

The *OTB Surface Treatment Technique Berlin GmbH & Co* is a medium size company in the metal working industry and part of the international operating company, *OTB Group*. The main location of the *OTB Group* is Berlin. In the industrial plating part, parts for the motor, electronics and telecommunications industries are treated. In the precious metal recycling department, with help of some home-made developments, gold, rhodium and platinum were being recovered. Another subsidiary manufactures surface thickness coating measuring instruments to testing standards.

The *OTB* is a specialist in the coating of connectors and lead frames, particularly for the selective coating and handling of complicated, three-dimensional bands. The selective surface treatment is done in: Au, Ag, Sn, SnPb, Ni, Pd, PdNi, Cu (cyan.) and Cu (acid).

OTB is also a manufacturer of plating and cleaning systems for continuous flow treatment. Plasma and high-pressure water cleaning processes were also installed for the cleaning of connectors, semiconductors and plastic coated chips. The pre-treatment and treatment of metallic components with the various quantities of, in some cases difficult metals for surface enhancing, created difficult conditions for the treatment of process waters.

With the split water streams that are treated in the batch effluent plant, these contain cyanide, cyanide free production as well as slightly contaminated surface water and special batches. The existing treatment plant, mainly based on chloride lime treatment, was not able to cope with these requirements without a high manual involvement, chemicals, reaction times and also special disposal measures such as tankering away.

To deal with the AOX and heavy metals content levels, a new technology was required. So early in 1991 with the help of a German supplier of UV-reactors, tests were made to improve the waste water problems. A dosing treatment, that was tried for a few minutes, drowned all hopes of a solution very quickly.

In the spring of 1998 the contact to *a.c.k.,* a company that had just been formed took place. The arguments from this company, because of a new way to build the reactors rather than just rely on UV exposure was the answer, and a rented trial unit over a few weeks would prove the viability of the process. The *Enviolet* reactor proved itself within a short period of time.

The treatment of surface water (*Tab. 3*) and *Bondal* posed no problems. Afterwards a series of tests for the treatment of *Ludigol-Stripper* followed to try the limits of the system. The system was also suitable for this application. In this way, during the rental period of the unit, a good proportion of the stored *Ludigol* was treated. Because of the changes in the legal disposal of *Ludigol* in Berlin, since mid 2000 it has to be disposed of as a dangerous substance.

In February 1999 an *Enviolet*® UV-installation with 12 kW and other process accessories for the retrofit of our batch treatment reactor, was installed by *OTB* (*Fig. 4*). After commissioning in the 2000, other additions were made such as pumps, pH controls, dirt traps, etc. The system is ideally suited for the so called *sour cyanide treatment* after the same name as the patent registered by the company *a.c.k*. and is routinely used for cyanide contaminated waters. Heavy metals, as in the past, are flocculated with sulphides in the presence of iron. Because of the corrosion resistant build of the UV-reactors, it can be cleaned with *chlorine acid*, normally every 8 weeks.

The cost situation for the cyanide treatment in *OTB* is shown in *Table 3* for 21 batches, as opposed to the old chlorine treatment versus the new UV-oxidation. For *OTB* the biggest benefit of the UV-oxidation is that the treat-

Tab. 3: Effluent data of waste water and concentrates of OTB

Average values	*84 m³ standard waste water (= 21 Batches)*	*8 m³ Ludigol Concentrate (= 2 Batches)*
Batch in m^3	4	4
Treatment time in h	6,5	24
Cyanid in mg/L (Initial)	9.500	30.000
Cyanid in mg/L (After treatment)	0,21	0,2
Consumption of H_2O_2 in L/m^3	27,3	100
Consumption of H_2SO_4 in L/m^3	58,2	160
Costs of "old" chlorine treatment in E (84 m^3)	6.784,- DM *	6.600,- DM
Costs of CyanoMat® in E (84 m^3)	3.168,- DM	687,70 DM
Savings by using CyanoMat®	53 %	90 %

* with 3 times longer treatment time of the conventional treatment

Fig. 4: CyanoMat®-system at OTB; Front: Enviolet®-UV-reactor, Backside: Treatment tank and process equipment

ment is much quicker than the old method and that the consent levels for AOX are within the limits.

OTB is planning to expand the system, this is possible because of the modular way the systems are constructed.

2.4 Tap Air Portugal (P)

By Project Engineer Emanuel Quintas (UNISIDA)

TAP Air Portugal is Portugal's leading airline with a world wide net. During the process of renovating the galvanizing repair shop of *Tap Air Portugal* in Lisbon, the effluent plant also needed to be upgraded. In the old effluent plant the treatment was carried out with chloride. This treatment, even with a 48-hour pretreatment of the stripper concentrates with electrolysis, still caused regular problems.

The consent levels fro cyanide, nickel, cadmium and silver still could only be achieved after a very long reaction times. For this a new cyanide treatment using UV was to be installed. On paper, this process was described as appropriate for the cyanide complexes [6, 7].

In the search by the systems manufacturer (*UNISIDA*), a number of UV-systems manufacturers were contacted and were given samples of the effluent so that an appropriate system could be proposed. The effluent to be treated was a combination of rinse waters and stripper concentrates (*Tab. 4*), unfortunately the trials up to then were not very successful because none of the companies involved believed the effluent could be treated successfully.

At a specialist waste water exhibition in 1999 *Tap Air Portugal* met a new specialist manufacturer who had just won the *Environmental Award* for the treatment of cyanide contaminated process waters with the use of UV-oxidation.

A test was made in the laboratory of the manufacturer using original effluent and the treatment proved successful. According to the German specialist there was no need for a trial at *Tap Air Portugal's* plant. After two visits to reference sites in Berlin and Schiltach, an order was placed for a system for *Tap Air*.

Tab. 4: Effluent data Tap Air Portugal

	Diluidos (Rinse waters)	*Concentrados (Stripper concentrate)*	*Values after Treatment*
Quantity in m^3/h	1,7	0,1	1,8
Quantity per day in m^3	10	0,5	10,5
Cyanide in mg/L	500	50.000	0.2
Nickel in mg/L	50	2.000	0.1 – 0.3
Silver in mg/L	30	-	0.1
Cadmium in mg/L	100	300	0.1 – 0.2
Copper in mg/L	10	-	0.1 – 0.3
Zinc in mg/L	100	300	0.2 – 0.3
Nitrobenenesulphonate in mg/L		40.000	below limit of detection
Colour	green - brown	deep red	none

The treatment of the effluent at *Tap Air* is done in a two stages process. At the pre-treatment stage the highly coloured and cloudy water is presented. Afterwards a dosing of hydrogen peroxide occurs to destroy the free cyanides. In the second stage a dosing of the catalysts and additional hydrogen peroxide and UV-treatment follows. During this stage the complex cyanides are destroyed first followed by the nitrobenzensulphonate from the stripper. The treated effluent is clear and free of metal complexes.

The German specialist manufacturer delivered the UV-system (*Fig. 5*) with the internal process technique to control the process, the engineering design for the whole system and the controls for the fully automated waste water treatment plant.

2.5 Shipley AG (CH)

By G. Baas

Shipley is a leading supplier of systems and chemicals for the surface treatment industry. Their own water treatment plant has some very hard tasks, it is required to treat the effluent of the chemical production, often containing many chemical complexes.

The treatment of the process waters posed over the years some very hard challenges to the effluent plant, and the operators to meet the consent levels. Also some considerable problems occurred when water containing cyanide and others containing EDTA and NTA were mixed. After installation of an *Enviolet* reactor (*Fig. 6*), the effluent could be sensibly treated and with measurable labour involvement. A very important benefit of the *Enviolet* reactor lies on the very low susceptibility of the ray treatment, the constant regulation of the reactor and an absolutely corrosion free choice of material. The UV-oxidation also

Fig. 5: CyanoMat®; front left 24kW Enviolet UV-reactor, back left treatment container for the principal oxidation with gas cleaning, back right treatment tank for pre-oxidation with integrated process technology

Tab. 5: Effluent data Shipley AG

	Waste water	*Values after precipitation*
Volume in m^3/d	6	-
Cyanide in mg/L	ca. 500	< 0,2
Copper in mg/L	ca. 1.000	< 1
Nickel in mg/L	ca. 500	< 1
Tin in mg/L	0 - 100	< 1
Zinc in mg/L	0 - 500	< 1
Iron in mg/L	0 - 500	< 5
Cadmium in mg/L	0 - 20	< 0,1
EDTA in mg/L	ca. 50	n.n.
NTA in mg/L	ca. 50	n.n.
Phosphor in mg/L	0 - 1.000	< 2
Time of treatment*)	approx. 10 h	-
Color	green, cloudy	colourless, clear

*) with performance 12 kW

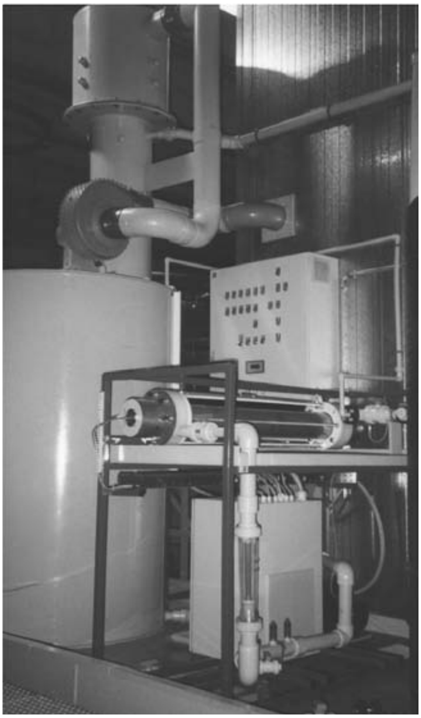

Fig. 6: CyanoMat® on the clients site for the treatment of complex metal cyanide waste waters including organic chelators like EDTA and NTA also

offers the benefit that the limits of AOX are also maintained since there is no reaction between chloride and organics contained in the water. Switzerland has a great deal of awareness to maintain these consent limits.

The cyanide limits as well as the consent levels for other metals has never been exceeded since the installation of the system. The mature way and the quality process in which the reactors are built means a very high efficiency that also has a positive effect on the savings of chemicals. The introduction of complex splitters was no longer required, and the quantities of precipitates and flocculants was reduced significantly.

Since the installation is working all environmental values for the relevant parameters cyanide an metals were kept (*Tab. 5*).

The lower salt content of the effluent also lead to a reduction in sludge produced, this also has a positive impact in the cost reduction of effluent disposal.

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Cyanomat®

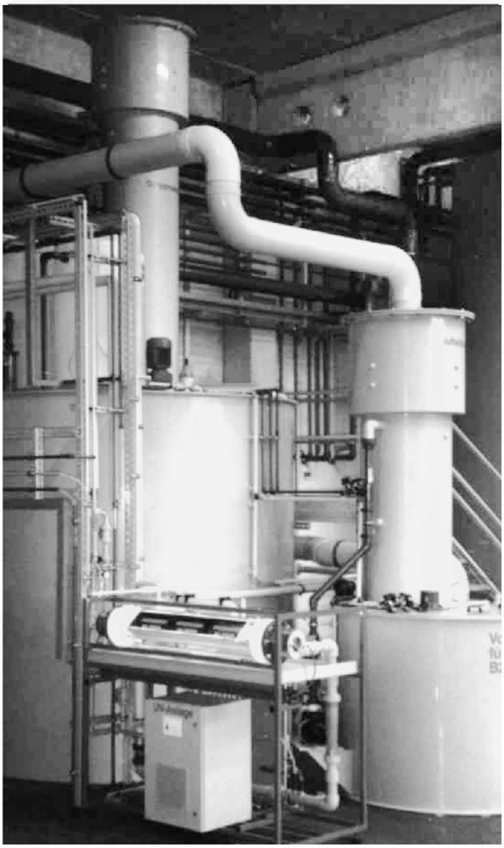

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Bild: Enviolet® UV - Anlage zur Zerstörung von Komplexbildnern. 10 m^3 - Chargen aus dem Bereich „Chemisch Nickel" werden abgearbeitet. Als typische Komplexbildner liegen EDTA, Citrate, Tartate, Benzoate und Ammoniumbiflourid vor. Die nachgeschaltete Fällung von Ni, Zn, Cu, Cr und Cd erfolgt sulfidfrei. Die Metallwerte sind nach der Fällung eingehalten.

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