Techno-Economical Comparison of Conventional Hydroxide Precipitation and Electrocoagulation for Heavy Metal Removal from Industrial Wastewater

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Treatment of industrial wastewater was performed by means of two neutralization/precipitation processes, using a conventional cascade line system and a novel electrocoagulation method (EC). The aim was to decrease the concentration of metals as Cu and Mn below 1mg/l. Effluents were provided by RTB-BOR, a Serbian copper mining and smelting complex being part of the EU funded project INTREAT. It focuses on the prevention of regional water resources contamination, where effluents containing heavy metals are currently discharged. Despite the fact that electrocoagulation was patented a century ago, there is no certainty about the operating mechanism behind this process, which is much the opposite case from chemical precipitation. The EC-method is described as the sum of two synergetic processes, working in parallel but acting separately one from another. On one hand, the coagulation process is considered as a stepwise mechanism based on fundamentals in the aqueous chemistry of metal cations. It starts with a hydrolysis, followed by condensation and complexation mechanisms, building colloidal conglomerates, which then act as the coagulant. On the other hand, the electrodeposition mechanism, working in parallel, ensures the efficiency of the process by removing heavy metals at lower pH values, acting as kind of a magnet for all foreign cations dissolved in the wastewater. Both processes have met discharge requirements, but significant differences related to applied mechanisms were observed, concerning material raw usage, energy demand and efficiency in terms of discharge requirements and operational costs among others. The EC-process has major advantages in comparison to the widespread chemical precipitation as in a cascade line system, which will be presented in this publication.

With fundings of the European Commission the project INTREAT “Integrated treatment of industrial wastes towards prevention of regional water resources contamination” addresses research and development of new and sustainable treatment methods for contaminated effluents [1]. Since chemical precipitation is the most common technology, a selective removal of heavy metals from metal containing effluents was achieved in a cascade line (CL) [2], especially designed for wastewater treatment and tested on industrial solutions from RTB-BOR, a Serbian mining and smelting complex. Getting acquainted with the need for environment-friendly and cost-effective processes, new ideas were explored in order to provide better answers to water reuse and metal recycling. Under this premise, a feasibility assessment of the electrocoagulation (EC) technology was carried out before [3], looking for an improvement to former attempts in this field, performed at IME for over the last years. Based on the attained know-how, the present study has been focused on a comparison between the conventional neutralization/precipitation process in a cascade line system and the electrocoagulation method, with regard to their technical and economical efficiency.

State of the art

Fundamentals of precipitation

Precipitation has been long used for heavy metal removal, based on the addition of chemical reagents to induce an increase of pH value, in order to manage a destabilization of the electrical charges responsible for the retention of such cations in leachates and metal containing effluents. There are several kinds of precipitation, which differ from the type of reagent used to drive the process. Those are:

- Hydroxide precipitation
- Sulfide precipitation
- Carbonate precipitation

To effectively precipitate metals, the control of pH is essential (especially

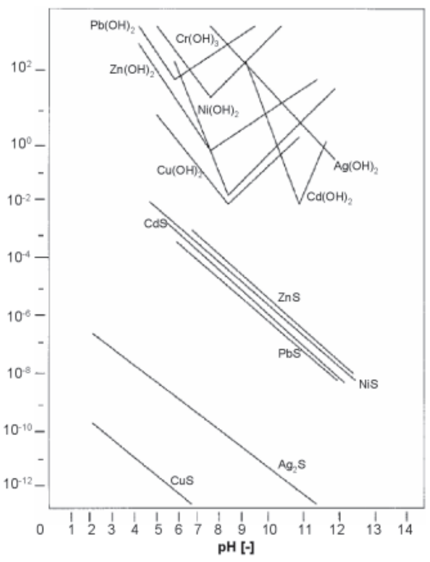

Fig. 1: Solubility of metal hydroxides and sulfides as function of pH [4]

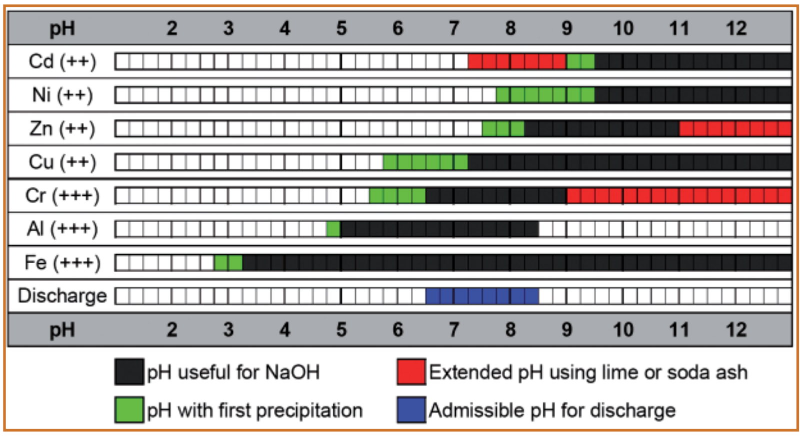

Fig. 2: pH ranges for metal precipitation with NaOH [6]

for hydroxide precipitation), as illustrated by the solubility curves for selected metal-hydroxides and metal-sulfides shown in Fig. 1 [4].

By definition, the solubility can be described as the amount of moles or milligrams of a solid, in this case the precipitate, which will dissolve in a liter of solution. Taking this into consideration, it is possible to determine the minimum (theoretic) concentration of soluble metals that will be present in the treated effluent after precipitation (Table 1) [5].

Facts about hydroxide precipitation

Despite some metals as lead, manganese, and silver may not be adequately treated by hydroxide precipitation, it is a well-established and simple technology, which has proven its ability to achieve the effluent limits for several metals, and it is well suited for automation [5]. Hydroxide precipitation of soluble heavy metals can be reached by adding alkali-precipitating agents, where ions are converted to relatively insoluble metal-hydroxide precipitates. The most common hydroxide-agents are:

- Caustic soda, NaOH
- Hydrated lime, $Ca(OH)_2$
- Magnesium hydroxide, $Mg(OH)_2$

After lime, caustic soda is the second most commonly used reagent, since it is approximately 100 times more soluble in water than lime (at 25 °C). Its main advantage relies on the rapidly dissociation into available hydroxyl-ions (OH^-) resulting in minimal holdup time, which may vary with rate of reaction and mixing. 15 to 20 minutes is a range for optimal and complete precipitation [5]. NaOH is easier to store, handle, and pump than is lime. In addition, it will not clog valves, form insoluble reaction products, or cause density control problems. Nevertheless, the main disadvantage of caustic is cost. Since NaOH is a monohydroxide, precipitating divalent metals require two parts of hydroxide per part of divalent metal precipitated, opposite to lime, which as dihydroxide base only requires one part hydroxide to do the same job [5].

However, in low flow applications where a reagent is selected on the basis of limited space, rapid reaction rates, and ease of handling, caustic is clearly superior, and since a major disadvantage of the lime process is the formation of large amounts of sludge, caustic becomes also a better choice when sludge disposal costs are high [5].

Metal	As hydroxide [mg/L]	As sulfide [mg/L]	As carbonate [mg/L]
Cadmium (Cd^{2+})	2.3×10^{-5}	6.7×10^{-10}	1.0×10^{-4}
Chromium (Cr^{3+})	8.4×10^{-4}	No precipitate	–
Cobalt (Co^{2+})	2.2×10^{-1}	1.0×10^{-8}	–
Copper (Cu^{2+})	2.2×10^{-2}	5.8×10^{-18}	–
Iron (Fe^{2+})	8.9×10^{-1}	3.4×10^{-5}	–
Lead (Pb^{2+})	2.1	3.8×10^{-9}	7.0×10^{-3}
Manganese (Mn^{2+})	1.2	2.1×10^{-3}	–
Mercury (Hg^{2+})	3.9×10^{-4}	9.0×10^{-20}	3.9×10^{-2}
Nickel (Ni^{2+})	6.9×10^{-3}	6.9×10^{-8}	1.9×10^{-1}
Silver (Ag^{+})	13.3	7.4×10^{-12}	2.1×10^{-1}
Tin (Sn^{2+})	1.1×10^{-4}	3.8×10^{-8}	–
Zinc (Zn^{2+})	1.1	2.3×10^{-7}	7.0×10^{-4}

Table 1: Theoretic solubility of selected metals in pure water (pH=7/25°C)[5]

Facts about electrocoagulation

Looking at old patents involving chemical precipitation [7] and electrocoagulation [8], chemical precipitation has been quite well characterized within a shorter period of time than EC. The characterization of metal removal and neutralization from effluents in the EC-process is a lot more complex. As a matter of fact, it involves two different processes acting in parallel. Due to this, there are only proposed models of how EC-process really works.

An EC-reactor is a simple arrangement of metal plates, based on so called sacrificial electrodes, which by means of electric current, get dissolved into water as charged ions, being responsible for neutralizing and required for destabilizing suspensions [3]. Production of polynuclear hydroxyl-aluminum particles is considered as a stepwise process involving deprotonation-dehydration mechanisms resulting in the formation of six-member rings, which may

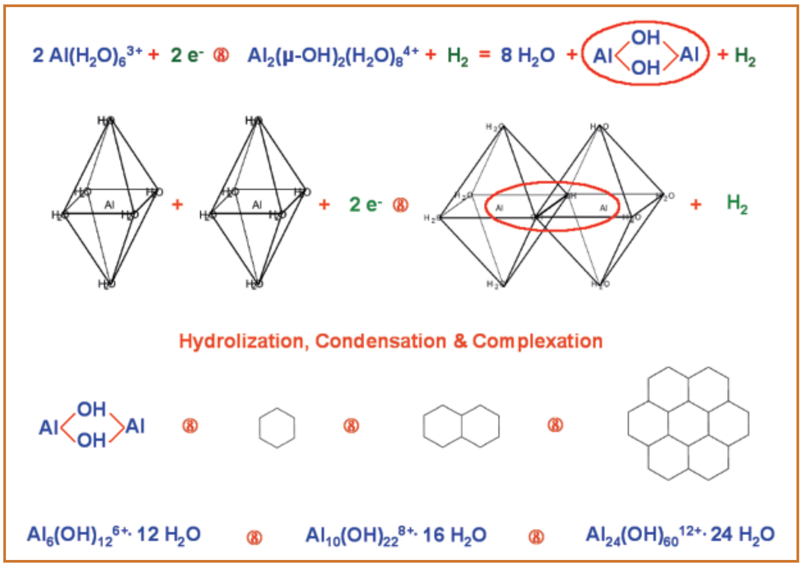

Fig. 3: Proposed EC-mechanism in aluminum-based systems [3]

further coalesce by the same mechanism [9] (Fig. 3).

The advantage of the EC-method relies on the fact of synergetic processes acting simultaneously. On one hand, metal plates, in this particular case solid aluminum, develop into a floc or coagulant in the presence of electric current within three stages [10] (Fig. 3): hydrolization (formula 1), followed by condensation (formula 2) and finally by complexation. On the other hand, hydrogen formation together with the electrochemical deposition occurring at the cathode, rapidly attract dissolved cations, which can be safely released afterwards just by inverting the polarity in order to recycle them from residual sludge.

$$Al_{(s)} + 6H_2O \rightarrow Al(H_2O)_6^{3+} + 3e^- \quad (1)$$

$$2Al(H_2O)_6^{3+} + 2e- \rightarrow Al_2(\mu\text{-}OH)_2(H_2O)_8^{4+} + H_2 \quad (2)$$

These two mechanisms ensure the efficiency and superiority of the EC-process over conventional techniques like chemical precipitation by removing heavy metals at lower pH values. A neutralization process is not required but it can be reached, since Al-hydroxide decreases hydrogen ion concentration, increasing then pH.

Nevertheless, there are some temperature issues which must be handled with care, since the solution gets saturated with Al-hydroxide and then it manages to dissolve itself again as the temperature increases [3]. However, this is not really a concern for discharge requirements, since economically speaking EC-process should never be run up to saturation.

Materials and methods used

Industrial wastewater used

Tests were conducted using metal containing wastewater (pH = 4.3) from copper production provided by RTB-BOR currently given to the Saraka stream in Serbia. RTB-BOR is a Serbian copper mining and smelting complex. Table 2 summarizes the composition of Saraka effluents.

The continuous cascade line precipitation system

Based on the wastewater composition, titration curves were carried out using 1L effluent, in order to determine the material raw usage (NaOH) by extrapolation, required to run the test in a larger scale. About 2L of NaOH-1M will be consumed to achieve precipitation of metals from 50L Saraka wastewater in 4 hours (continuous operation).

Table 3 summarizes the process parameters involving hydroxide precipitation in the continuous cascade line.

Fig. 4 presents the 3 reactor used in the precipitation line. The most important parts are:

1. Reactor-1: 10L glass vessel (pH = 4.3 – 5.7)
2. Reactor-2: 10L glass vessel (pH = 5.7 – 7.3)
3. Reactor-3: 10L glass vessel (pH = 7.3 – 9.3)
4. Agent dosing: solenoid pumps BT4a 1005 ProMinent
5. Stirring: e-drives with speed control (300 rpm)
6. pH-Meter: Mettler-Toledo 2100e glass electrode
7. Storage tank: 200L capacity for untreated wastewater
8. Product tank: 200L capacity for treated effluents

The retention time in each of the three reactors was about 15 minutes, while some particles were deposited at the bottom by means of centrifugation (300 rpm). Contrary to the significant

Element [Symbol]	Copper [Cu]	Aluminum [Al]	Manganese [Mn]	Sulfate [SO_4^{2-}]
Concentration [mg/L]	50	13	6	560

Table 2: Composition of Saraka wastewater from RTB-Bor

Parameter	Final pH	Reaction time	Waste water treated	Flow rate	Active agent	Agent used	Energy demand
value	9.3	45min	9.4L	12.5 L/h	NaOH	0.375L	60 Wh

Table 3: Parameters for neutralization tests using NaOH-1M in a continuous 3 reactor precipitation line

Fig. 4: Continuous 3 reactor precipitation line at IME RWTH-Aachen, Germany

change in pH (from 4.3 up to 9.3), a considerable change in temperature was not observed (ΔT = 6 °C).

Electrocoagulation (EC) system

Regarding the test conducted on the EC-system, suitable parameters were found at former test series reported on a feasibility study carried out prior to this work [3]. Concerning the EC-reactor, 12 aluminum electrodes with 8mm gap and powered by a supply unit at 17A were used (total electrode area = 0.57 m^2, current density = 30A/m^2). Table 4 summarizes important implemented parameters involving the electrocoagulation method.

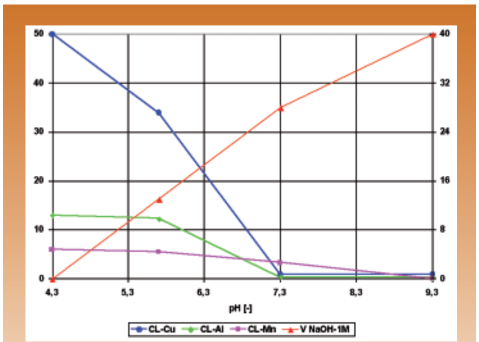

Fig. 5: Metal removal and neutralization effect using NaOH-1M in a continuous 3 reactor precipitation line

Fig. 6 presents the used electrocoagulation set up. In regard to used equipment, the most important parts are:

1. EC-reactor: 10L-plexiglass tank (200 x 210 x 245 mm^3)
2. Power supply: EA-PS7016-400, 0-16V DC, 0-40A
3. Conductivity: WTW-LF197-S with probe head
4. pH meter: WTW-pH197i with T-indicator
5. Power contr.: Protek 506 with serial data port
6. Data acquis.: software from Protek on IBM T23
7. Pretreatment: 10L capacity with magnetic stirrer
8. Filtration unit: paper-based with sludge bifurcation

Determination of metal concentrations

In order to compare the efficiencies of heavy metal removal from both processes, samples were taken before and after treatment, then analyses were done via ICP-OES method in the chemical lab at IME.

Fig. 6: Electrocoagulation system at IME RWTH-Aachen, Germany

Results and Discussion

Process temperature and pH values were measured in real time and sampling was done every 15 minutes. Table 5 and 6 summarize all results observed during tests.

Effect of pH-value on metal removal

Since heavy metals are retained in metallurgical effluents due to electrical charges, opposite charged ions are required to neutralize the suspension, in order to stimulate destabilization and precipitate dissolved cations [11]. While the standard hydroxide precipitation process relies only on that principle, the EC-process introduces an electrochemical deposition, which rapidly attracts dissolved cations within the first minutes of operation (Fig. 7). This explains the remarkable difference in metal removal efficiency at low pH values (EC = 93% average against CL = 15% at a pH of about 5.6).

Parameter	Final pH	Reaction time	Waste water treated	Flow rate	Active agent	Agent used	Energy demand
value	7.1	45min	9.4L	12.5 L/h	Al plates	9.4 g	125 Wh

Table 4: Parameters for neutralization/precipitation tests using an EC-system

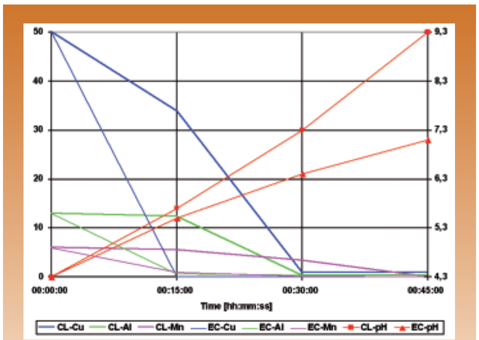

Fig. 7: Effect of pH-value on metal removal

Efficiency of copper removal

Fig. 8 shows the positive effect of electrocoagulation on Cu-removal. As it can be seen from the copper concentrations, not only from the operating time, but also from material raw usage (NaOH). Nearly 100% of copper cations were removed in the EC-process within the first 15 minutes (final content: 4 µg/L).

Efficiency of aluminum removal

Regarding aluminum, although there is quite a difference within the first minutes of operation, both processes have reached the same level (0.3mg/L). However, from the material raw usage and operational issues, they still allow to vote for the EC-method as the cost-effective one.

The test results demonstrated also that hydrolization of aluminum plates in wastewater did not represent any environmental concern, regarding an increment of Al-cations in effluents, since most of them (97.7%) remained in sludge (about 30% Al in the dried sludge).

Efficiency of manganese removal

The removal of Mn from the investigated wastewater forces the standard neutralization process to exceed the neutral range (pH > 7), in order to secure the removal below the discharge requirements (<1 mg/L). In doing so, not only economical issues are to be considered, but also ecological concerns, since such alkaline solutions represent a risk to the environment [12] (6.5 < pH < 8.5 stipulated by law, see Fig. 2). Compared to this the EC-process was able to reduce the manganese content below 20 µg/L after 45 minutes, five times less than in the conventional CL-process in the same time (0.1 mg/L, pH = 9.3), without producing alkaline effluents (pH = 7.1), reaching a maximum removal rate of 99.7%.

Time [min]	pH [-]	T [°C]	Cu [mg/l]	Cu [%]	Al [mg/l]	Al [%]	Mn [mg/l]	Mn [%]
0	4.3	20	50	0	13	0	6	0
15/R1	5.7	26	34	32	12.3	5.4	5.5	8.3
30/R2	7.3	27	0.9	98.2	0.4	96.9	3.3	45
45/R3	9.3	25	0.9	98.2	0.3	97.7	0.1	98.3

Table 5: Results (contents and removal efficiencies) from the three-reactor precipitation line (R1-R2-R3)

Time [min]	pH [-]	T [°C]	Cu [mg/l]	Cu [%]	Al [mg/l]	Al [%]	Mn [mg/l]	Mn [%]
0	4.3	20	50	0	13	0	6	0
15	5.5	25	0.009	99.9	0.57	95.6	0.97	84
30	6.4	29	0.004	99.9	0.36	97.2	0.22	97
45	7.1	33	0.004	99.9	0.3	97.7	0.02	99.7

Table 6: Results from the electrocoagulation-process

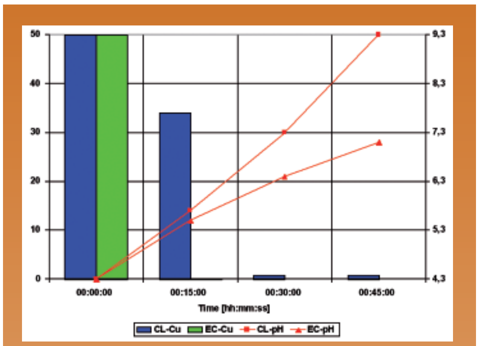

Fig. 8: Effect of neutralization on copper removal (CL: cascade line, continuously operated; EC: electrocoagulation)

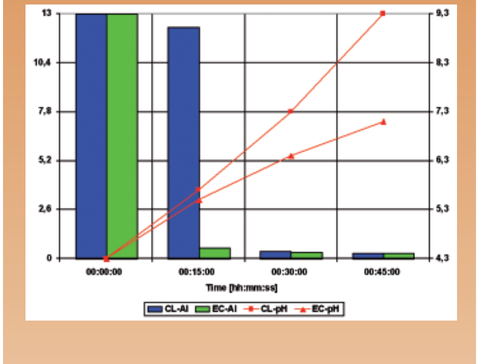

Fig. 9: Effect of neutralization on aluminum removal

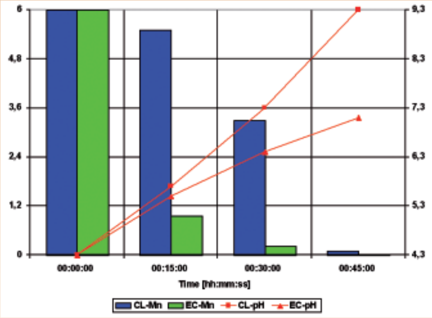

Fig. 10: Effect of neutralization on manganese removal

Effect of neutralization on temperature

While in the standard neutralization process the increase of temperature obeys only to a neutralization reaction, electrocoagulation is a lot more complex. Neutralization induces here changes of electrical properties from the solution, leading to higher energy consumption as the conductivity decreases along the process (Fig. 11).

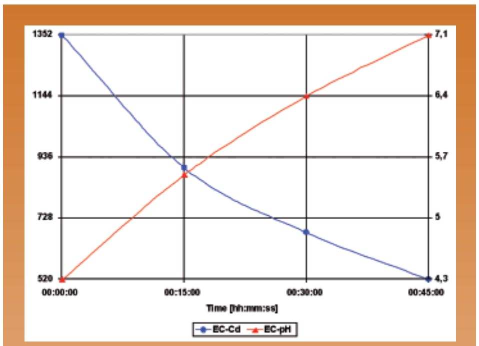

Fig. 11: Effect of pH-value (degree of neutralization) on wastewater conductivity [3]

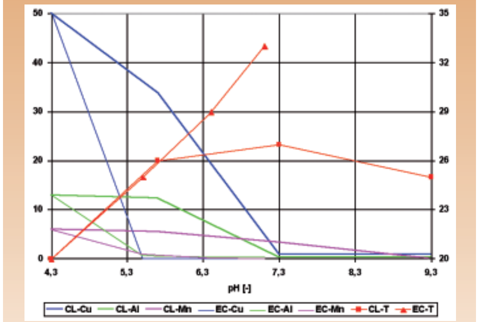

Fig. 12: Effect of neutralization degree on temperature

It forces the system to dissipate more power in the very same space, in the form of heat as reported before in [3].
Fig. 12 shows temperature change for both CL- and EC-process during neutralization.

Required time for neutralization

Based on the kind of bounding, pH value may be influenced by the presence of sulfate anions like $CuSO_4$, which opposite to some other bounds like $NaSO_4$, may acidize the solution and provide ideal conditions for cations to remain dissolved. Although the EC-process allows promptly metal removal, neutralization based on hydroxides, whether using $Al(OH)$ or $NaOH$ to precipitate heavy metals, requires extra time to decrease hydrogen ion concentration, reaching pH = 7 in 30 to 45 min (Fig. 7).

Element [%]	Cu	Al	Mn	Na
from CL-system	1.06	0.29	0.11	12.4
from EC-system	1.18	29.4	0,13	N.D.

Table 7: Composition in weight [%] of air dried sludges

Amount and quality of precipitates

After treatment, the dried solid residue was weighted and analyzed. While nearly 0.4 g/L waste was recovered from water in the standard neutralization process, EC produced 1 g/L of dried sludge due to the anodic dissolution. Even though EC-process produces roughly twice more sludge than precipitation using NaOH (one major advantage of caustic over lime), regarding treatment costs, 11 EUR/m^3 for NaOH precipitation, in comparison to 6 EUR/m^3 for electrolytic Al-hydroxide from EC-process (see Table 8), it is likely to conclude that the hydroxide precipitation costs are almost twice more than from electrocoagulation. Table 7 shows element concentrations found in sludges.
Fig. 13 and 14 show the difference in appearance of sludges recovered from the standard and the EC-process.

Energy and operational facts

In regard to the used parameters and considering an effective flow rate of 12.5 L/h for both processes in order to meet current discharge requirements (metal concentrations below 1mg/L), a rough estimation for the treatment of 110 m^3/y, was assumed for both investigated methods. Table 8 compares energy demand and operational facts (neglecting assets and personal costs), between standard chemical precipitation using NaOH-1M vs. electrolytic dosage of Al-hydroxide in the EC-process.
The concentration analyses carried out via ICP-OES (Fig. 15) and the outlined technical and economical facts provide enough evidence about the superiority of EC-technology over standard hydroxide precipitation as seen on Fig. 16 (EC > 99% vs. CL > 98% average removal rates).

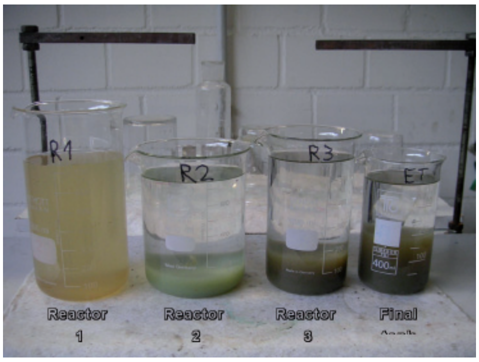

Fig. 13: Sludge from the continuous cascade line reactors

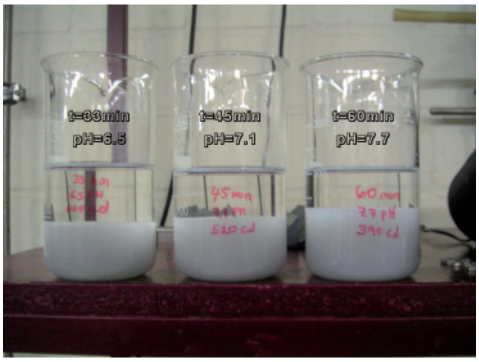

Fig. 14: Sludge from EC-reactor

Conclusions and Outlook

Based on the presented results, it can be concluded that both EC and CL-process have successfully removed metals (Cu, Al, Mn) in effluents below 1mg/L. However, EC-technology proved to be more environment-friendly with outstanding cost-efficiency potentials compared to hydroxide precipitation. Technically speaking, the EC-process achieved not only higher removal rates (in the µg/L range) but also a better neutralization of effluents within equal period of time (nearly 45 minutes), providing better conditions for discharge requirements (neutral pH).
Economically speaking, the EC-process seem to be more effective, taking into account the material raw cost, which for NaOH is more expensive.

Parameter	Cascade Line	Electrocoagulation
Effective flow rate	12.5 L/h	12.5 L/h
Annual capacity	110 m^3/y	110 m^3/y
Material added	Sodium liquor (NaOH)	Aluminum plates (Al)
Material cost	0.25 €/L (NaOH-1M)	4 €/kg (Al-plates)
Material used / m^3	40L (NaOH-1M) / m^3	1kg (Al) / m^3
Material cost / m^3	10 €/m^3	4 €/m^3
Annual material cost	1100 €/y	440 €/y
Power consumption	60W (agitators, pumps)	125W (EC-reactor)
Energy demand / m^3	4.8 kWh/m^3	10 kWh/m^3
Annual energy cost	106 €/y (≈0.2 €/kWh)	220 €/y (≈0.2 €/kWh)
Annual total cost	1206 €/y	660 €/y
Treatment cost / m^3	11 €/m^3	6 €/m^3

Table 8: Energy demand and operational facts of the standard chemical neutralization and the EC process

While treatment costs per cubic meter using hydroxide precipitation ascend to 11 EUR, the very same amount of wastewater can be successfully treated with even better results for 6 EUR.

The use and/or recycling of the collected sludge have to be investigated in the near future. With nearly 30% of aluminum being present in the EC-sludge, chances for metal recycling, in order to improve the sustainability of this method, may play an important role in the proliferation of this method, not only for industrial, but it may also be interesting for municipal sewage application instead of using aluminum sulfate in phosphorus removal.

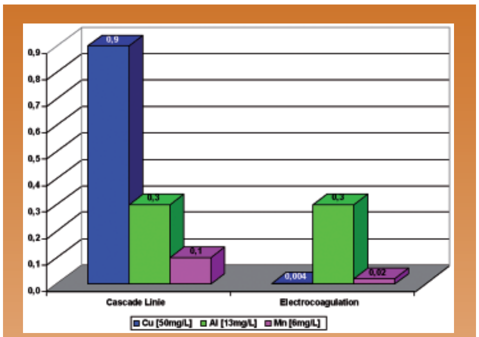

Fig. 15: Final concentrations after treatment (ICP-OES)

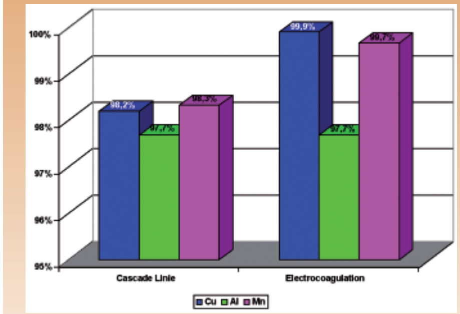

Fig. 16: Overall metal removal rates after treatment

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