

A new procedure for recovering heavy metals in industrial wastewater

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Abstract

The usual way to treat heavy metal containing industrial wastewater leads to large amounts of hydroxide sludge. In general, the concentration of the non-ferrous metals in the sludge is too low for an efficient recovery of these elements and in consequence, these secondary raw materials dissipate. New procedures were developed to treat wastewater from traces up to 25 g/l heavy metals like Cu, Ni, Zn, Mn, Pb, Sn, Pd and Ag. Using the modified ferrite process with $Fe/M = 2/1$ specific products free of hydroxide can be produced. The precipitates are in most cases a mixture of heavy metal ferrite, oxides or zero-valent metal. By reduction of iron ratio, it is also possible to produce doped oxides without by-products. A new treatment method is the so-called Lt-delafoosite, with $Fe/M = 1/1$. The application of the treatment methods for five different rinsing waters from the electroplating industry showed that in each case the recovery rate is higher than 99.9%. A simplified calculation was performed for a Pd activator bath and for three rinsing water loaded with Sn and Pd, Cu or Ni. Referring to a model volume of 1000 l wastewater with weekly exchange, the loss of metal by dissipation per year sums up to approx. 1 ton, based on typical rinsing waters, showing 1.5 g/l to 3 g/l Cu or Ni or rather 15 g/l Cu. Further ecological and commercial benefit of this procedure is the drastic reduction in waste volumes. Additional costs for transport and disposal of the neutralisation sludge can be avoided.

Keywords: heavy metal, Cu, Ni, Pd, Sn, wastewater treatment, ferrite process, Lt-delafoosite, recovery potential, nanoparticle.

1 Introduction

Huge amounts of industrial wastewater and effluents occur, e.g. in the electroplating industry. Generally, they are treated with lime or caustic soda in order to precipitate the heavy metals. Mostly the resulting sludge are deposited in landfills. In Germany 95% of the nonferrous metals get lost by dissipation, and only 5% of the voluminous sludge is processed to recover the heavy metals [1]. Noble metals, e.g. Pd, are used as activators to produce reactive surfaces. The recovery of these elements out of an aqueous solution is of outermost interest.

We developed a new procedure to treat wastewater with heavy metal concentrations up to 25 g/l at temperatures $< 90^{\circ}\text{C}$. After treatment, the purified wastewater complies the threshold values for environmental regulations. By applying our method, we are able to avoid the usual formation of hydroxide sludge. Moreover, we can recover these heavy metals as oxides or even zero-valent metals. We succeeded to treat heavy metals (Cu, Ni, Zn, Mn, Sn, Ag and Pd) in both, synthetic and real wastewaters. Below we present our concept using the example of copper and nickel containing rinsing water from electroplating industry. Additionally, we present our first results for the treatment of an activator bath to recover Pd and Sn.

2 Treatment of heavy metal containing industrial waste water

2.1 State of the art

Various techniques exist to remove heavy metals from wastewater. The most applied principles of operation are precipitation and ion exchange [2]. Both methods produce metal bearing residues (e.g. highly voluminous lime sludge, exhausted ion exchange resins, highly metal loaded deionizer regeneration wastewater), which are barely used for the recovery of metals [e.g. 1]. The lion's share of these residues is hazardous waste, representing the end of pipe treatment.

A well-known method for metal recovery is based on electrolysis. For most technical implementations of these electrowinning systems, the lower threshold for an efficient application is a minimum metal concentration of 30 mg/l and 50 mg/l respectively. Special techniques (e.g. using mesh cathode cells, fluidised or packed bed cells) provide metal recovery up to lower metal contents of 0.5 mg/l or rather 0.1 mg/l [2]. However, all these techniques based on electrolysis are suffering from very high operating costs and are only applied if recovered metals can be offered competitive and profitable on the metals exchange. In combination to the previously introduced methods, oxidising and reducing reagents respectively are in use, e.g. for treatment of metal bearing effluents loaded with problematic substances, like cyanides, uranium leachates (U^{4+}) or hexavalent chromium (Cr^{6+}).

A low-tech alternative to deplete metals in wastewater is based on wetland metal mineralisation. However, the efficiency of heavy metal removal with this biogenic method is quite low compared to the above-mentioned methods [2]. Further techniques, using metal accumulation microorganisms (e.g. bacteria,

algae, yeasts and fungi), are interesting alternatives but play a minor role in industrial treatment of metal containing effluents.

2.2 Model plant

To demonstrate our concept, we use a model plant from an electroplating industry with three different types of baths, comprising Pd as activator, Ni and Cu, each followed by a rinsing cascade (Figure 1).

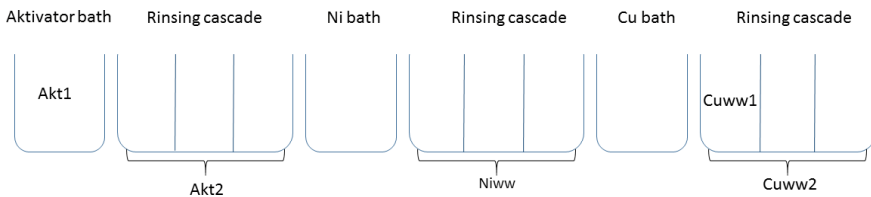


Figure 1: A model plant in electroplating industry with five different types of wastewater.

At the beginning, the surface of plastics needs a pre-treatment to enable the deposition of the chemical agent Ni on the plastics as an anti-rust layer below the next Ni, Cu and Cr layers. For example, Pd is used as an activator to form the needed catalytic sites on the surface. Sample Akt1 was collected from a Pd activator bath in the electroplating industry. Sample Akt2 is a rinsing water accrued after the Pd activator bath (Akt1). Wastewater Niww is a mixed sample collected from a multistage rinsing cascade after the Ni bath. Wastewater Cuww1 was sampled from the first rinsing tank directly after the Cu bath and Cuww2 is mixed sample collected from a multistage rinsing cascade.

The heavy metal concentrations of samples Akt1, Akt2, Niww, Cuww1 and Cuww2 are summarized in Table 1. The chemical analysis was performed by ICP-OES or AAS.

Table 1: Heavy metal concentrations [mg/l] in wastewater from electroplating industry: Akt 1 and Akt 2 are wastewater from Pd activator bath and rinsing cascade, respectively, Cuww1 is a rinsing water from the first rinsing cascade after the Cu bath whereas Niww and Cuww2 are mixed rinsing water from multistage rinsing cascades. n.d. means not determined.

Sample	Concentration [mg/l]						
	Pd	Sn	Cu	Zn	Fe	Cr	Ni
Akt1	78	2600	12	52	67	34	< 1
Akt2	7	648	3	28	4	8	< 1
Niww	n.d.	0.5.	< 0.1	< 0.1	< 0.1	< 0.5	1423
Cuww1	n.d.	n.d.	15560	13	3	6	245
Cuww2	n.d.	n.d.	3010	3	1	3	53

2.3 How large is the potential of dissipated heavy metals?

The introduction of a new environmental technology for an industrial application rarely depends alone on the ecological value of the procedure. It is generally expected that this method is economically profitable. Therefore, an assessment of the potential of this new process was conducted. Figure 1 shows a model plant for electroplating which was used as base for a simplified model calculation. Starting point for our estimation are our high recovery rates for heavy metals, ranging between 99.5% and 100% (see Section 3). The potential of the heavy metals was determined based on the main contaminants (Sn, Ni and Cu). The concentration of heavy metals in wastewater from the multistage rinsing cascades is low ≤ 3 g/l. For wastewater from the first rinsing cascade the concentration can be higher than 10 g/l. Due to the high market value, the potential of lower concentrated Pd (activator bath: 78 mg/l and rinsing water: 7 mg/l) was also calculated.

The production parameters differ extremely dependent on the individual plant sizes. For example, industrial tanks used for electroplating typically contain volumes of about 2 m³; a typical rinsing water cascade contains capacities of 6 m³. Typical tank volumes of small companies comprise minor sizes of about 300 l. For better comparability, applicable for both, small enterprises and industrial plants, our data are calculated for a model volume of 1000 l. The usual production conditions with a weekly exchange of water from a multistage rinsing cascade were used as basis for the estimation of the annual amount of wastewater (see Table 2).

Table 2: Recovery potential of heavy and noble metals based on 1000 l bath or rinsing water.

Sample	Metal	Concen- -tration	Recovery rate	Recovery of metal ¹⁾	Annual recovery ²⁾	Value ^{3,4)}
		[mg/l]	[%]	[kg/1000L]	[kg/year]	[€/1000L]
Akt 1	Pd	78	> 99.98	0.078		1378.16
Akt 1	Sn	2600	97.04 – 99.98	2.561		6.15
						[€/year]
Akt 2	Pd	7	> 99.98	0.007	0.364	6063.03
Akt 2	Sn	648	97.04 – 99.98	0.638	33.194	79.67
Niww1	Ni	1423	99.9 – 99.99	1.422	73.955	406.75
Cuww1	Cu	15560	> 99.98 – 100	15.558	809.039	2427.12
Cuww2	Cu	3010	> 99.98 – 100	3.010	156.504	469.51

¹⁾Average values; standard deviation: > 0.2%

²⁾Weekly bath exchange: 52x per year

³⁾Scrap value on 21.04.2016 [3]: Sn 2400.00 €/t, Ni 5500.00 €/t, Cu 3000. 00 €/t

⁴⁾Market value for purchase of solid Pd on 21.04.2016 [4]: 501.00 €/oz., 1666.00/100g.

Our data clearly demonstrate that over the course of a year small amounts of non-ferrous metals in the wastewater of the three different rinsing cascades, add up to a loss in the range of 265 kg. If metal is recovered from a highly loaded rinsing water (> 10 g/l), the amount of highly concentrated heavy metals increases considerably. Based on 1000 l, the cumulative potential of Cu recovery is 809 kg (Cuww1) in comparison to 156 kg for the rinsing water (Cuww2).

2.3.1 Benefit of the recovery of heavy metals

Reflecting the resale value, the potential of recovered heavy metals from rinsing waters was determined on base of the (lowest) scrap values in order to include recycling costs (see Table 2). Following considerations are based on 1000 l wastewater treatment. The annual benefit of the simplified model plant for electroplating is in the range of 500 € (scrap value [3]) for Ni and Cu, respectively. Considering highly loaded rinsing water (15 g/l) the potential for copper recovery raises to 2500 € (scrap value). In absence of scrap values for Palladium, proceeds realized from purchase of solid Pd [4] are included in the simplified cost-benefit evaluation.

The annual potential for Pd recovered from rinsing water is approx. 33 kg or about 6000 €. The purchase value of recoverable Pd and Sn from 1000 l activator bath is about 1400 €. In total, referring to the depicted model plant with one activator bath and three types of heavy metal rinsing water systems (Pd, Ni, Cu), sums up to a loss by dissipation of approx. 260 kg of metal, representing foregone revenues in the range of about 8500 €.

2.3.2 Additional profit for companies

It is notable to point out to further enormous saving potentials. By applying our method of wastewater treatment, the actual costs incurred by transport and disposal of highly voluminous neutralisation sludge will be obsolete. The annual volume is within the range of 100 t/a and 500 t/a for smaller facilities and may exceed 10000 t/a for industrial plants. The cost structure is very inhomogeneous, due to its dependence on several parameters, e.g. volume (total amount), metal content (recycling capability/toxicity), transport distance. In Germany in 2015, costs summarised for both, transport and disposal, were in average in the range of 100 €/t to 200 €/t.

3 New methodology

3.1 Development of a new technology

The new technology presented here is based on the ferrite process published by Okuda and coworkers for the first time and several other studies using this methodology, e.g. [5, 6]. Accordingly, Fe^{2+} ions are added to the wastewater containing the heavy metals M in the ratio $\text{Fe}^{2+}/\text{M} = 2/1$. After alkalisation hydroxides precipitate and later, as a result of oxidation of the hydroxides, heavy metal (M) is incorporated in the spinel structure (ferrite). Our investigations, however, showed clearly that e.g. Cu is only partly incorporated in the copper

ferrite solid solution with magnetite [7]. But we recognised that by modification of the ferrite process two goals can be obtained: effective wastewater purification even for highly concentrated wastewater up to 20 g/l and recovery of secondary raw materials due to low voluminous residues. The recovery rates of the heavy metals are very high, generally between 99.5 and 100%. Moreover, we can design a procedure to gain the heavy metals as marketable products. Depending on type and concentration of the heavy metals in the wastewater and adjustment of the Fe/M ratio in the solution different precipitates are achieved. Reaction conditions applied during precipitation and ageing procedure control the composition of the final residues. The main interphase is green rust (GR); it represents one of the major phases in fresh precipitates.

In consequence, we developed three concepts to produce heavy metal containing nanoparticles. Option 1) high-Fe system [7] and option 2) low-Fe system [8] are based on the modified ferrite process. Option 3) comprises a new concept called LT-delafoosite process [9–11]. Following case studies with possible treatment concepts for the five real wastewater are presented (see Figure 1 and Table 1).

3.2 Experimental setup

Following setup was used to perform the experiments with real wastewater from electroplating industry (Figure 2). The experiments were carried out in a 3-neck glass flask, heated by a special Al-block to guarantee homogeneous heat distribution. After a reaction temperature of 40°C or 70°C was reached, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (VWR, analytical grade) was added to the solution. Then the pH was adjusted to a value between 9 and 11. The solution was continuously heated and stirred during these steps. An aliquot of the fresh sample the solution containing the precipitates was stored in a closed vessel either at room temperature

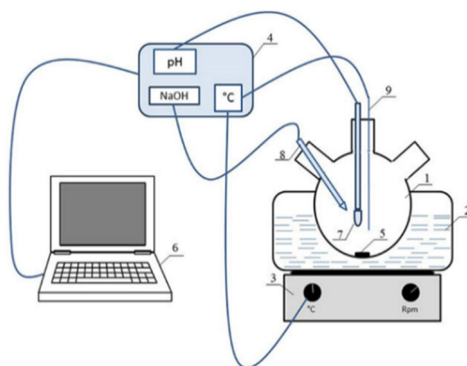


Figure 2: Experimental setup consisting of: (1) reaction vessel, (2) Al-block, (3) heating plate, (4) alkalisiation unit Titrator TL 7000 (SI Analytics), (5) stirrer, (6) controlling station, (7) pH-electrode, (8) titration needle and (9) thermocouple connected to the alkalisiation unit and the heating plate.

or at elevated temperature. The precipitates were filtrated and washed 3 times with high-purity water and dried at room temperature for 12–24 h.

Samples are named according to the following convention: “used wastewater” _ “Fe-content” _ “reaction temperature” _ “reaction pH” _ “ageing time”.

The extension “rt”, denotes an ageing at room temperature. The abbreviation for the “Fe-content” is “m” for a medium amount of Fe added, “h” for a high amount and “vh” for a very high amount of added Fe.

3.3 Analytical methods

The concentration of heavy metal in the solution was measured by ICP-OES or AAS. Various analytical methods were used to detect the partly amorphous precipitates. Phase identification was performed by X-ray powder diffraction (XRD) with Stoe Stadi and GE Seifert XRD 3003 TT. Fourier Transform Infrared Spectroscopy (FTIR) using a Bruker Equinox 55 was performed to identify X-ray amorphous phases. Magnetic measurements were carried out, using a Variable Field Translation Balance (VFTB) by Petersen Instruments. Morphologies of precipitates were studied by scanning electron microscopy (SEM) using a GEMINI 98 manufactured by LEP (now Zeiss) and by transmission electron microscopy (TEM) using a JEOL JEM-2100F microscope.

4 Case studies

4.1 Copper loaded wastewater

4.1.1 Treatment by modified ferrite process: high-Fe and low-Fe option

The Fe/Cu ratio was varied from $< 0.8/1$ (low-Fe option) up to $2/1$ (high-Fe option). Further parameters, which control the final composition of the solid phases, are the quantity of initial copper in the solution and ageing time. The variation of the solid phases is shown in Figure 3.

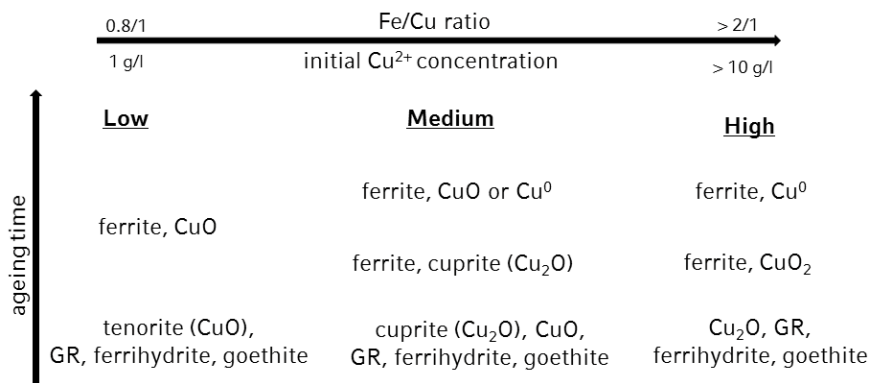


Figure 3: Scheme showing the variation of the product phases with varying initial Cu concentration, Fe/Cu ratio and ageing time.

At high Fe/Cu ratio 2/1 and high Cu concentrations in the solution (> 10 g/l) a mixture of $(\text{Cu,Fe})\text{Fe}_2\text{O}_4$ (a solid solution of copper ferrite and magnetite) and zero valent Cu^0 precipitates. With ageing, the amount of Cu_2O increases at the expense of ferrite and zero valent Cu^0 (Figure 3). At low Cu-concentrations in the solution and medium amount of added Fe we obtained Cu_2O , CuO and ferrite. By further decreasing the added Fe content to the wastewater the amount of CuO increases. Table 3 shows that it is possible to precipitate Fe doped CuO as mono phase by the low-Fe concept.

Table 3: Phases of sample series Cuww2. Those observed with XRD are marked with X/x and phases observed with FTIR are marked with F/f. Capital letters stand for a high amount, small letters for a low amount of the appropriate phase.

Sample	Phases				
	CuO	Cu_2O	GR	$\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$	Fe_2O_3
Cuww2_0.5_f	x		f	f	f
Cuww2_0.5_24h	X	x			
Cuww2_0.25_f	X		f	f	
Cuww2_0.25_24h	X				
Cuww2_0.125_f	X			f	
Cuww2_0.125_24h	X				
Cuww2_0.06_f	X				
Cuww2_0.06_24h	X				

4.1.2 Treatment by Lt-delafofossite process

Another option presents a totally new synthesis route for delafossite CuFeO_2 at Fe/Cu ratio 1/1 solely by precipitation and ageing at temperatures between 50°C and 90°C , called Lt-delafofossite process [9, 10]. The adaptation of this process on real wastewater was successfully performed with initial copper concentration > 15 g/l, typical for the first tank of the rinsing cascade and < 5 g/l, typical for multistage rinsing systems [11]. The reached water purification rates are exclusively $\geq 99.99\%$. After 16 h of ageing the residues consists of pure, nano-sized delafossite without any additional phases.

4.2 Nickel loaded wastewater

Table 4 summarizes the precipitated phases of two sample series Niww. Reaction temperatures $< 70^\circ\text{C}$ and reaction pH values of ≥ 10.5 promote the formation of $\text{Ni}(\text{OH})_2$. By specific adjustment of the reaction conditions of the ferrite process, we succeeded to decrease the $\text{Ni}(\text{OH})_2$ content and to increase the ferrite component in the precipitates (see Figure 4). The achieved water purification rate for Ni is exclusively $\geq 99.9\%$ independent of reaction temperature and pH value.

In contrast to reaction pH we observed no relation between reaction temperatures and the purification rates. The lowest Ni concentrations were detected in fresh solutions after treatment with reaction pH values of ≥ 9 . Better water purification rates in comparison to fresh filtrates were achieved after treatment with reaction pH of 8 and 8.5 and ageing of the samples for at least 24 h.

In sample series Niww, with low initial Ni^{2+} concentration < 1.5 g/l, we succeeded the precipitation of ferrite as main phase at temperatures $\geq 70^\circ\text{C}$, a reaction pH value of 9.5 and ageing at elevated temperatures for 24 h. After treatment of wastewater Niww the Ni concentration dropped from 1423 mg/l to ≤ 0.24 mg/l. At optimal conditions, the Ni concentration dropped down to ≤ 0.11 mg/l. This corresponds to a recovery rate of $\geq 99.99\%$. It was also possible to remove the other minor elements (< 4 mg/l) completely from the solution.

The fact that both, IR-bands and reflection positions in XRD pattern, are shifted, indicates that Ni is preferentially incorporated into the ferrite structure.

Table 4: Phases of sample series niww. Phases detected by XRD are marked with X, phases analyzed by FTIR with Fm and traces with x and f.

Sample	Phases			
	Ferrite	$\text{Ni}(\text{OH})_2$	GR	$\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$
Niww_9.5_50_f		x, f	F	F
Niww_9.5_50_24h	x, f	X, f	f	f
Niww_9.5_70_f	f	x, f	F	F
Niww_9.5_70_24h	X, F		f	f
Niww_9.5_70_7d	X, F	x, f		f
Niww_9.5_70_7d_rt	X, F	x, f	f	F
Niww_9.5_90_f	x, f	x, f	f	F
Niww_9.5_90_24h	X, F			f
Niww_10.5_70_f	x, f	f	f	F
Niww_10.5_70_24h	X, F	X, F		f

4.3 Palladium and tin loaded wastewater

The concentration of Pd in activator bath is 78 mg/l and shows 7 mg/l in rinsing water. Furthermore, minor amounts of Cu, Zn and Cr have to be treated.

Within this study 12 sample series using Pd activator bath and the corresponding rinsing wastewater were performed. The experiments were carried out at pH values of 9 and 11, temperatures of 40°C and 70°C and under adjustment of three different Fe/M ratios.

For both samples (Akt1 and Akt2), highest purification rates were achieved at a reaction pH value of 9. Afterwards the Pd concentration dropped to < 0.1 mg/l; this corresponds to a recovery rate of $\geq 99.98\%$. At higher reaction pH ≥ 10 the Pd

concentration in the purified water increased (≈ 0.5 mg/l for sample Akt1). The purification rate for Sn was lower, ranging between 97.04% and 99.98%. The minor elements Fe, Cr and Cu were removed to $\approx 99\%$. Only in case of Zn in sample Akt1, the recovery rate was $\approx 55\%$ independent of the reaction conditions.

The first mineralogical investigation of sample Akt1 showed that the main controlling parameters are temperature, ageing conditions and added Fe^{2+} content. Depending on the experimental conditions, we observed four different phase assemblages in the residues:

- 1) After ageing, the residues obtained by precipitation with a high Fe-content, at pH 9 and temperatures between 40 and 70°C mainly consist of jeanbandyite $\text{FeSnO}(\text{OH})_5$ (sample Akt_h_70_9 and Akt_h_40_9). A minor amount of ferrite compound is detectable independent of reaction temperature and ageing conditions.
- 2) With decreasing temperature, the ferrite content in the sample markedly increases. For samples precipitated at a low temperature of 40 °C, pH value of 9 and addition of “medium” Fe contents, the residues consist of ferrite as the only crystalline phase (Akt_m_40_9).
- 3) Reaction temperature of 70°C and 24 h ageing time promotes the phase mixture of $\text{FeSnO}(\text{OH})_5$, ferrite, SnO and an additional phase we cannot identify so far (Akt_m_70_9_1d).
- 4) After ageing the reaction products of option 3 at room temperature (Akt_m_70_9_1d_rt), the sample consists mainly of the “unknown” phase. Additionally, small contents of $\text{FeSnO}(\text{OH})_5$ and ferrite are observable.

5 Discussion and conclusion

In this study, we presented possible treatment methods for 4 different wastewaters and 1 process water bath from electroplating industry companies. The results show that it is possible to purify effectively the wastewater in compliance with the legal requirements for environmental regulations. Moreover, it is unambiguously possible to recover heavy metals. In contrast to traditional water treatment methods of industrial effluents, the precipitate phases have only negligible amounts of metal hydroxides and therefore they have the potential for a profitable marketability. This new treatment procedure can also be used to treat highly loaded rinsing water with heavy metals > 10 g/l.

One outstanding aspect of our treatment method is the precipitation of metal oxides in the sense of product design, like nano-sized delafossite (CuFeO_2) or doped CuO. Under certain reaction conditions, heavy metals can also be recovered as zero-valent metals. An overview of possible product lines gives Figure 4.

A simplified model plant including one Pd containing activator bath, and three rising water cascades after Pd, Cu and Ni bath was used as base for considerations about the recovering potential of heavy metals in electroplating industry. Referring to a model volume of 1000 l wastewater, the loss of the non-ferric metals by dissipation sums up to approx. 250 kg per year. In case of 15 g/l copper, the recovery potential raises to 800 kg per year.

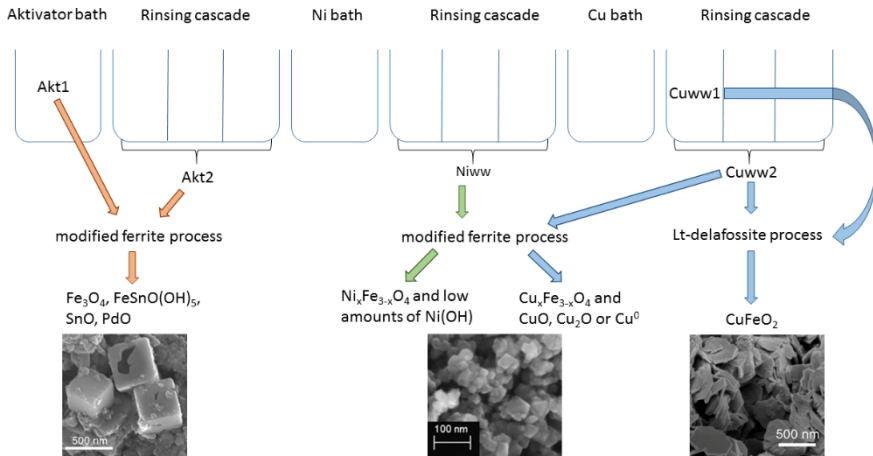


Figure 4: Overview of phase assemblages obtained after treatment of the modified ferrite process or Lt-delafofossite process.

In general, all precipitates are highly suitable for recycling and reprocessing of heavy metals as secondary raw materials in a smelter. A more innovative approach is the production of nanocrystals in terms of upcycling, by synthesising valuable phases like delafossite or doped oxides with much higher value. These phases are highly demanded (raw) materials for several technical applications. Our results show that it is possible to produce them directly from the effluents.

Another ecological and commercial benefit for companies is the drastic reduction in waste volumes. Additional costs for transport and disposal of the neutralization sludge can be avoided.

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