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HEAVY METALS REMOVAL

HYCOR NET RM
HYCOR EBCL

PRODUCTS PROFILES

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Plating, galvanic, quench towers, incinerators wastewater contains heavy metals, and suspended solids at levels hazardous to the environment and pose risks to public health.

Heavy metals, in particular, are of great concern due to their toxicity. Because of the high toxicity and corrosiveness of plating waste streams, plating facilities are required to treat wastewater prior to discharge in accordance with National Regulations

In the Table are reported the allowed metals discharge limits in Italian Law.

Numero parametro	**SOSTANZE**	**unità di misura**	**Scarico in acque superficiali**	**Scarico in rete fognatura (*)**
9	Alluminio	mg/L	≤ 1	≤ 2,0
10	Arsenico	mg/L	≤ 0,5	≤ 0,5
11	Bario	mg/L	≤ 20	-
12	Boro	mg/L	≤ 2	≤ 4
13	Cadmio	mg/L	≤ 0,02	≤ 0,02
14	Cromo totale	mg/L	≤ 2	≤ 4
15	Cromo VI	mg/L	≤ 0,2	≤ 0,20
16	Ferro	mg/L	≤ 2	≤ 4
17	Manganese	mg/L	≤ 2	≤ 4
18	Mercurio	mg/L	≤ 0,005	≤ 0,005
19	Nichel	mg/L	≤ 2	≤ 4
20	Piombo	mg/L	≤ 0,2	≤ 0,3
21	Rame	mg/L	≤ 0,1	≤ 0,4
22	Selenio	mg/L	≤ 0,03	≤ 0,03
23	Stagno	mg/L	≤ 10	
24	Zinco	mg/L	≤ 0,5	≤ 1,0

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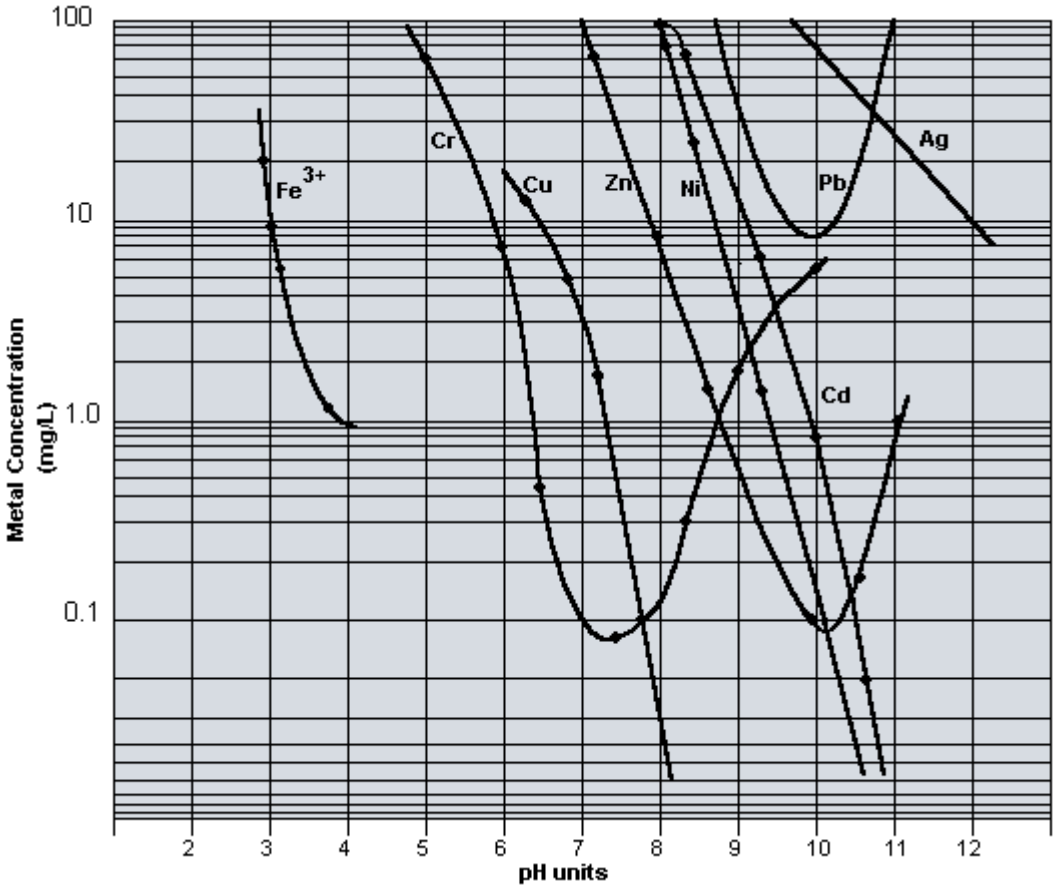
Especially galvanic and electronic industry (printed circuits) wastewater treatments must tackle the problem of the presence of heavy metals in final discharge.

The plating process typically involves, alkaline cleaning, acid pickling, plating, and rinsing. Copious amounts of wastewater are generated through these steps, especially during rinsing. Additionally, batch dumping spent acid and cleaning solutions contributes to the complexity of waste treatment.

With greater quantities of wastewater produced and discharge standards becoming increasingly more stringent, there is a need for more efficient and cost-effective methods for removing heavy metals.

Conventionally, precipitation has been the method most often used to remove heavy metals. Of the few precipitation methods, hydroxide and sulphide are the two main methods currently used, and hydroxide precipitation is by far the most widely used method. However, this method does not ensure total compliance for the various metals present in the waste stream, since all metal hydroxides do not completely precipitate at a single pH.

The most common used method to remove soluble metal ions from solution is to precipitate the ion as a metal hydroxide. The process is readily automated and controlled by a simple pH controller. By raising the pH value of a solution with a common alkaline material such as lime, or sodium hydroxide the corresponding metallic hydroxide compounds become insoluble and precipitate from solution. Below is a metal hydroxide solubility curve showing the solubility of the common heavy metal ions and their respective solubility versus pH.



If copper is reviewed, it is seen that at a pH of 6 copper has a solubility of 20 mg/l and at a pH of 8.0, the solubility is 0.05 mg/l.

Nickel has a similar curve but it occurs at 3 pH points high. At a pH of 8.0 nickel has a solubility of 70 mg/l and at a pH of 10.2 the solubility is 0.1 mg/l.

Several metals such as chromium and zinc are amphoteric, being soluble at both alkaline and acid conditions. Chromium reaches its least theoretical chromium solubility of 0.08 at pH of 7.5.

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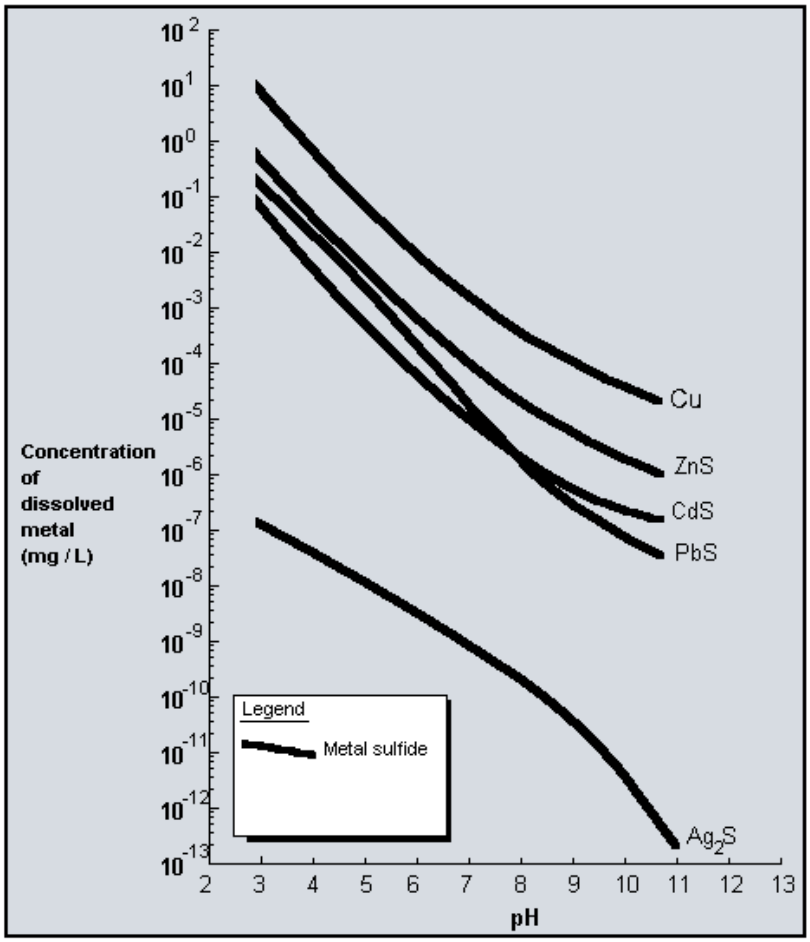
If both chromium and nickel are present a pH value that precipitates both ions must be chosen. It is common to utilize a pH of 9.0 - 9.5 to precipitate both metals.
The theoretical solubility usually does not exist in practice. Metallic coagulant such as ferric chloride or aluminum sulfate are generally used to accelerate the coagulation and precipitation of the heavy metals. Even when not added they are present from other metal processing solutions such as the pickling bath. Ferric hydroxide and/or aluminum hydroxide precipitate and tend to form co-precipitate with nickel and chromium. The net is a metallic ion concentration lower than would be predicted from the solubility curve.
If chromium must be precipitated to a level less than 0.5 mg/l the pH must be operated at 7.0-8.0. If nickel is present it must be precipitated with sulfide as the metallic sulfide ion. Chromium does not form insoluble sulfide precipitates and must be precipitated as the hydroxide at 7.0 - 8.0.
Attached is the heavy metal sulfide solubility curves. The sulfide solubility is several orders of magnitude lower than the comparable hydroxide.



Additionally, the presence of chelating or complexing agents, oil and grease, synergistic reactions and high concentrations of dissolved solids can result in diminished efficiency of precipitation.
The hydroxide precipitation treatment involves precipitation of heavy metal hydroxide(s), flocculation with a polymeric material, settling and discharge of treated effluent. Such a technique is time consuming and requires extensive setup. Each step takes place in a separate tank, and the entire treatment requires several pH adjustments and the use of chemicals such as acids, alum, ferrous and ferric salts, lime or caustic and polymeric flocculent. In addition, the process generates large volumes of sludge/waste that require disposal and is normally hazardous due to the high concentrations of heavy metals. Hazardous waste must undergo treatment to render it suitable for disposal. This treatment adds to the already high cost of wastewater treatment and places an extra burden on treatment facilities.

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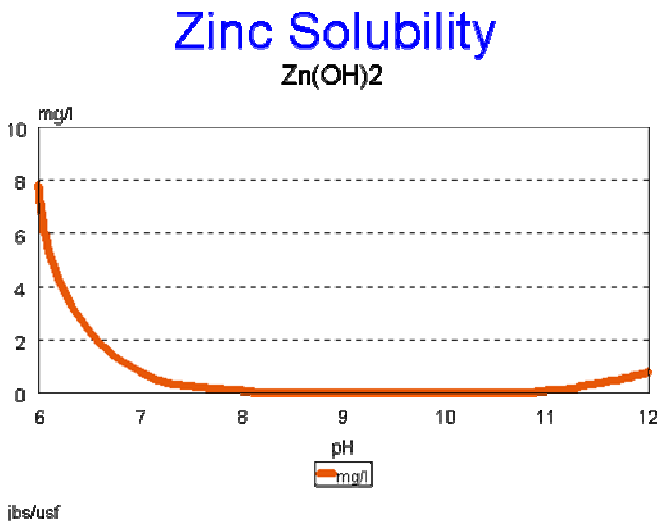
INTECNA developed two new additives for heavy metals removal :

HYCOR EBCL	for Zinc removal
HYCOR NET RM	for Copper, Lead, Cadmium

Zinc is most often found in plating, galvanizing and roller coating operations. In plating shops, the zinc is often complexed with cyanide and the cyanide must be treated to free the zinc before precipitation can occur. Like copper, zinc can be precipitated as the hydroxide, carbonate, phosphate or sulfide. Unlike copper, it cannot be reduced to the metal at low enough concentrations to meet most treated water requirements. Finally, it can be removed by ion exchange in methods similar to copper.

The equipment used for treating zinc is the same as used for treating copper with the exception that zinc cannot be removed by reduction to the metal.



The problem connected with the Zinc removal is the formation in alkaline environment of micro-flocks , often with colloidal form and such flocks are not totally retained by conventional anionic polymers.
The action of **HYCOR EBCL** is a quick hydrolysis in alkaline wastewater with contemporarily formation of voluminous flocks with strong absorbing capacity.
On the surface of such flocks, Zinc Hydroxide will be absorbed and the precipitation is more efficient and the final treated wastewater is totally clarified.
A typical Zinc Hydroxide precipitation with **HYCOR EBCL** an anionic polymer is reported in the photo

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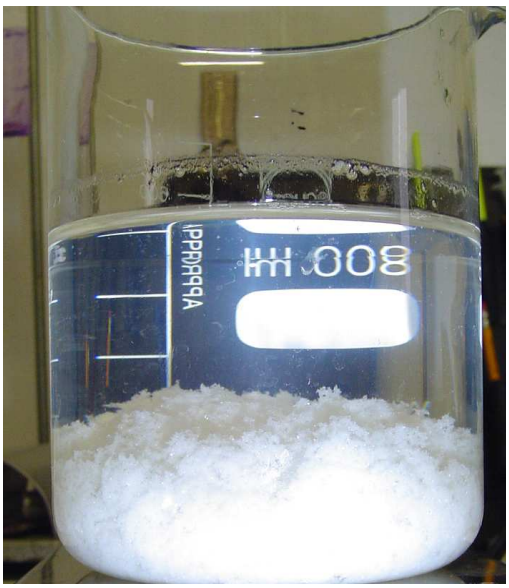

The product **HYCOR EBCL** reacts simultaneously with metals, suspended solids and oil and grease to form large, dense flock that settles efficiently, resulting in improved performance of the clarifier, shorter filter press cycles and drier filter press cakes.
The treatment proved very economical and versatile, and the product is easy to work with and safe to handle. The new treatment produces effluents that meet or exceed discharge standards and generates non-hazardous waste

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The action of **HYCOR NET RM** is based on the capacity of the product to form a complex with heavy metals with Solubility Product in the dimension of 10 exp – 40.
The complex formation in heavy metal removal has been identified as an effective when used in conjunction with coagulant and flocculant technology. This new method should be viewed as a three-step approach involving the following:

Producing insoluble metal compounds using organic precipitants

Coagulating these precipitates for more effective removal rates

Flocculating the fine particles to promote rapid and complete settling

HYCOR NET RM , when added to the waste stream, form a stable micro-flock that is neither dependent on pH nor affected by chelated or other complexed metals.
While experiments have show metals removal to trace amounts using organic precipitants alone, it may be more economical to adjust the pH of the wastewater to allow hydroxide precipitation of the most abundant metal and then further reduce the remaining metal ions using the organic precipitant product.
Organic precipitant addition is controlled by the use of a stoichiometric ratio for each particular metal ion to be removed

In the following graphic is reported the removal of Cu, Ni, Cd in the range below 2 ppm vs ppm of HYCOR NET RM

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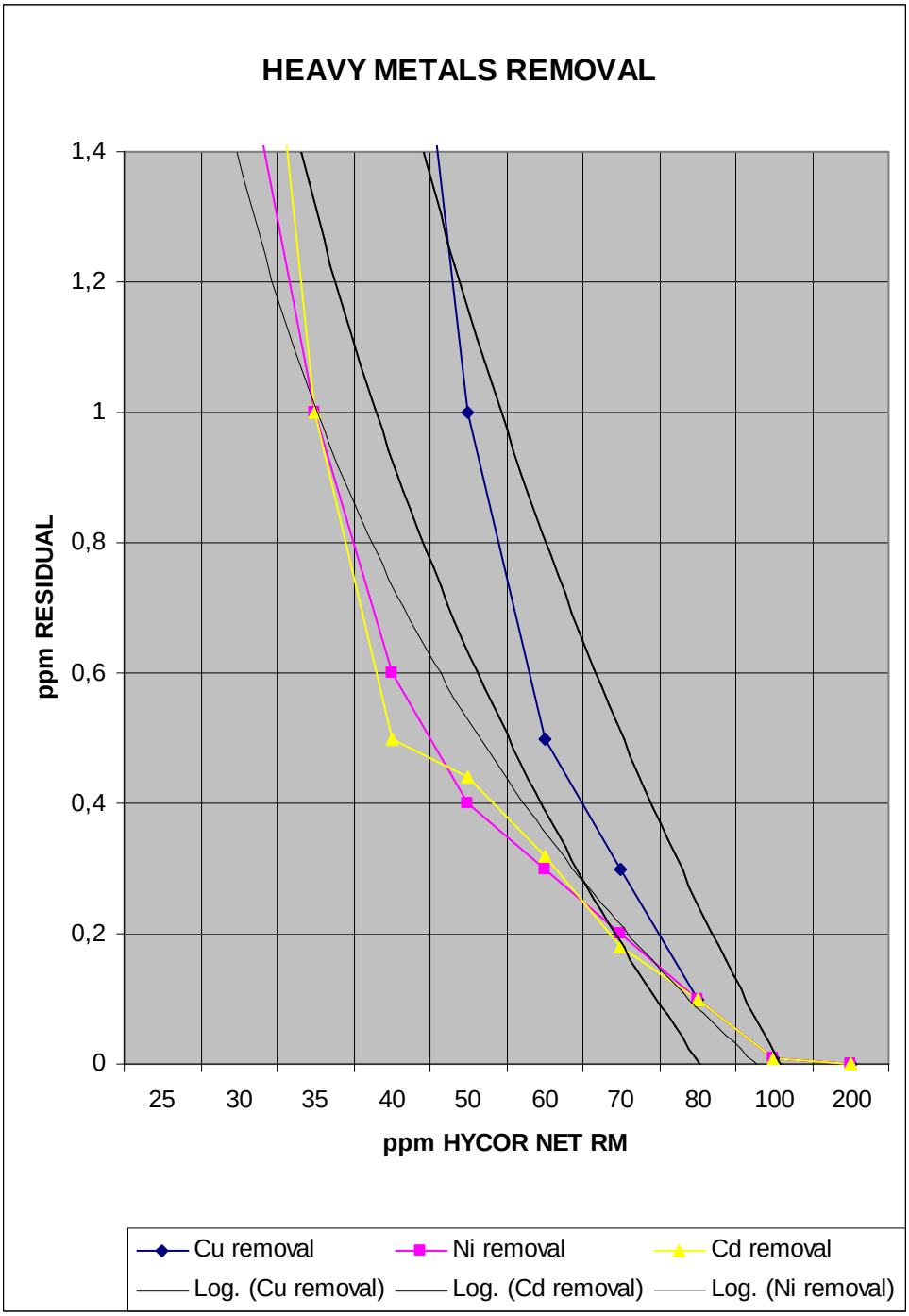
HEAVY METALS REMOVAL
ppm RESIDUAL
1,4
1,2
1
0,8
0,6
0,4
0,2
0
25
30
35
40
50
60
70
80
100
200
ppm HYCOR NET RM
Cu removal
Ni removal
Cd removal
Log. (Cu removal)
Log. (Cd removal)
Log. (Ni removal)