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D. WILMS*, L. PAWŁOWSKI**, M. KOTOWSKI**,
J. VAN DIJK***, M. SCHÖLLER***

METAL RECOVERY FROM SPENT BATHS IN A FLUIDIZED-BED REACTOR

1. INTRODUCTION

A new system for the recovery of heavy metals (Zn, Cu, Ni, Cd, Co, Hg) from wastewater of the electroplating and chemical industry by crystallization of heavy metal carbonates in a fluidized-bed reactor has been developed by DHV Consulting Engineers, The Netherlands, in cooperation with the Catolic University of Leuven, Belgium, where the fundamental parameters of the crystallization of metal carbonates were investigated.

Contrary to conventional wastewater treatment methods (hydroxide precipitation) no sludge is produced, but instead pure pellets of metal carbonate. These pellets can be reused in the electro-plating and chemical industry. The plant is very compact and has low investment and operational costs. All kinds of wastewaters with a metal influent concentration of 10 ppm to 100 g/dm^3 can be treated. Depending on the kind of metal an effluent quality in the ppm–ppb range can be obtained.

2. SYSTEM DESCRIPTION

The principle of a pellet reactor is shown in fig. 1. The reactor consists of a cylindrical vessel, partially filled with suitable seed material, e.g., filter sand. The fluid velocity in the reactor is so high (40–100 m/h) that the grains are kept in suspension and that cementing of the grains is prevented. A carbonate solution dosed into the reactor causes the metal carbonates (e.g., $ZnCO_3$, $NiCO_3$, $CuCO_3$) to crystallize on the seed material. The reaction takes place very quickly, so that only a small reactor volume is needed. A 3 m high reactor with a diameter of 20 cm can treat a flow of 1.2 m^3/h.

The reaction results in growth of the grains and after some time the larger pellets must be removed from the bed. These metal carbonates are pure and can be reused after dissolving the pellets in acid; the carbonate then escapes as CO_2, while the sand core can be used in the reactor again as seed material.

* Catholic University of Leuven, Leuven, Belgium.
** Technical University of Lublin, 20-618 Lublin, ul. Nadbystrzycka 40, Poland.
*** DHV, Amersfoort.

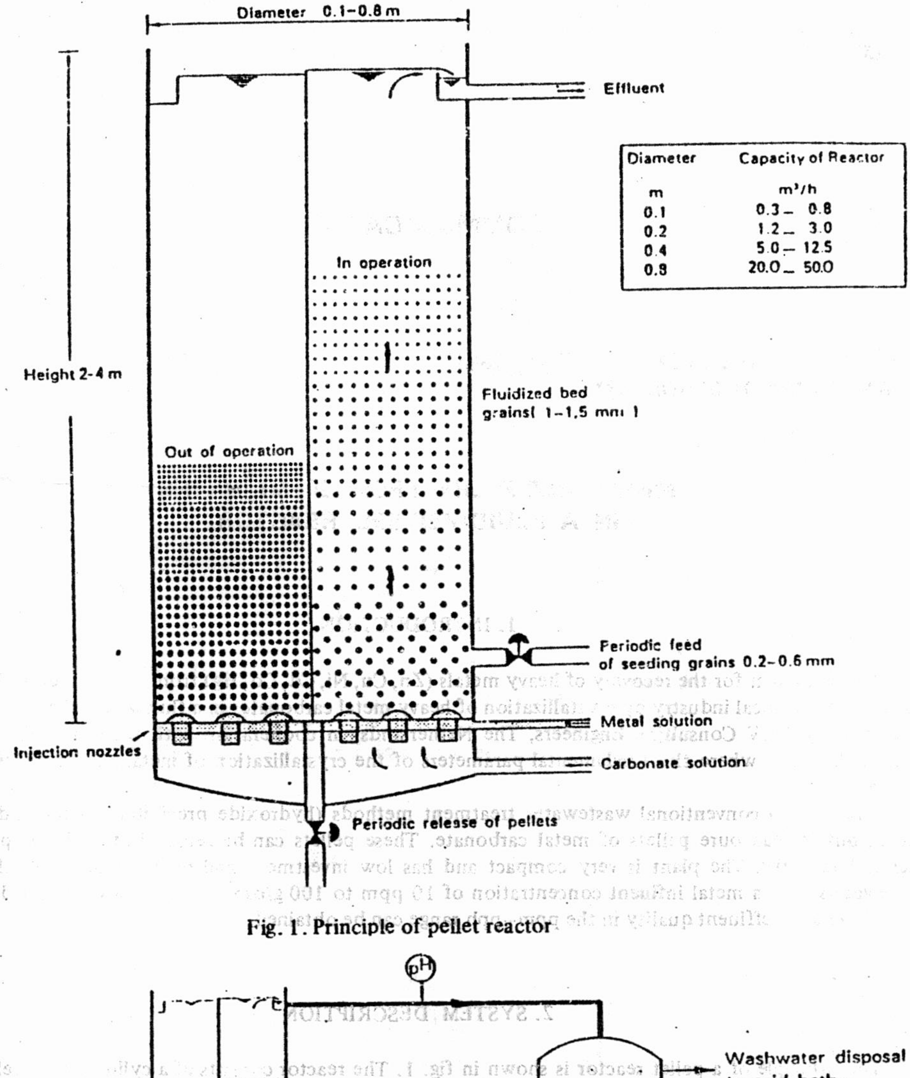

Fig. 1. Principle of pellet reactor

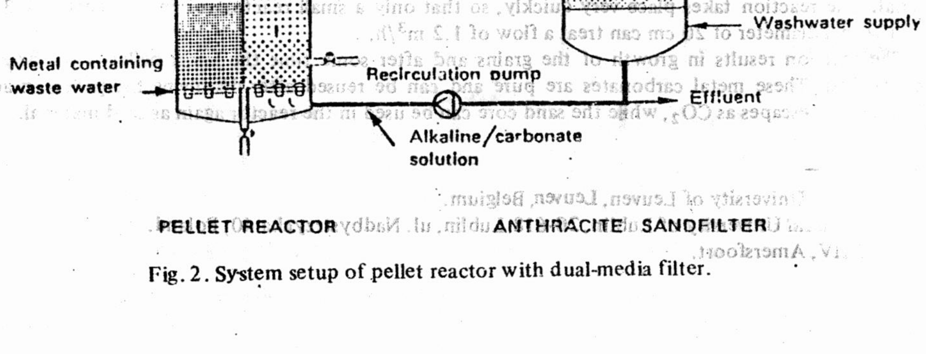

Fig. 2. System setup of pellet reactor with dual-media filter.

In principle crystallization of heavy metal carbonates in a pellet reactor has the following advantages:

1. The pellets produced are pure and can be reused. This provides a saving in the purchase costs of heavy metals.

2. The system is very compact because the pellet reactor operates with a high fluid velocity (75–125 m/h). By adapting the recirculation ratio to the metal influent concentration, wastewaters with a very wide concentration range can be treated.

3. No chemical sludge is produced, whereas the sludge production from a hydroxide plant if used as further treatment is greatly reduced.

In practice, a sturdy plant with very good results can be achieved. The greater part of the heavy metals crystallizes onto the grains. A minor part will remain in the effluent in the form of small suspended particles of metal carbonate or metal hydroxide (carry-over). These suspended particles are filtered in an anthracite–sand filter (fig. 2).

Wastewaters with a metal content of 10 ppm to 100 g/dm^3 can be treated. In the case of a low metal content no recycle or a low recycle ratio is required, while at a high metal content a high recycle ratio is required.

The most important parameters in the process are the pH of crystallization and the ratio of total carbonic acid, C_T, over metal concentration. The higher the pH, the more distinct the tendency of amorphous metal hydroxide to precipitate; the lower the pH, the more sodium carbonate has to be added in order to obtain a sufficient high concentration of CO_3^{2-}, so that the solubility product of the metal carbonate will be exceeded. Other important parameters of the process are the recirculation rate, and the size and the amount of pellets in the reactor: these parameters influence the degree of mixing, the stability of fluidization and the capacity of the reactor.

3. RESULTS

An intensive investigation of the crystallization of copper carbonate has been carried out at the Catholic University of Leuven. In the pH-range of 6.5–8.5 and at a C_T/Cu dose ratio of 1.5–5.3, a very high copper removal rate has been obtained. The reactor has been fed with a 1300 ppm copper solution and produces an effluent concentration of 0.2–2 ppm. The produced pellets consist of malachite ($Cu_2CO_3(OH)_2$). The crystallization reaction time is a few seconds and the height of the crystallization zone is 20–40 cm.

Table 1 gives some process conditions and results from pilot plant experiments on baths of different plating industries.

Table 1

Process conditions and results

Baths plating industry	Process conditions			Results		
	pH	CT/Me dose ratio (mol/mol)	Recircu-lation ratio	Me influent (ppm)	Me reactor (ppm)	Effluent filter (ppm)
Zn	8–9	2–3	0–10	40–100	< 1	–
Ni	9.5–11	2–3	4–50	400–4000	<10	< 1
Cu	7–8	2–3	10–20	700–3000	< 1	–
Co	8–9	2–3	20–60	7000	< 1	–

The effluent from the plant will have different destinations, depending on the system selected: Discharge to the main sewer or to a hydroxide precipitation plant. In come cases (Zn, Cu) direct discharge may be considered. In other cases (Ni) if a hydroxide precipitation plant is available, further treatment is indicated. However, the use of chemicals and the production of sludge by the hydroxide precipitation will be greatly reduced.

Recirculation to a drag-out bath (process integration). In this case, the carbonate can escape into the air as CO_2, provided there is sufficient acid in the bath.

The backwash water from the sand filter can be returned to an acid drag-out or plating bath where the carry-over is dissolved; it can then still be abstracted in the pellet reactor in the succeeding cycle.

In principle the system can treat a number of flows containing metals, such as plating baths, drag-out baths, conversion baths, pickling baths and rinsing water. The heavy metals (Zn, Ni, Cu, Co, Cd, Mn, Ba, Sr, Ag, Pb and Hg) can in principle be abstracted as crystals of metal carbonate. Chromium does not form a carbonate salt and therefore cannot be abstracted in this way.

4. PRINCIPLE

Metal (II)-ions can form compact carbonate crystals. The carbonate salts of most heavy metals have low solubility, as shown in tab. 2. In practice, reaction conditions must be selected such as to allow the solubility product of the metal carbonate to be exceeded slightly (if too much, spontaneous nucleation may take place which results in formation of carry-over), whereas the solubility product of the metal hydroxide should not be exceeded: metal hydroxides are not crystalline and form a wet voluminous sludge (as in fact occurs in hydroxide precipitation plants).

Table 2

Solubility products of metal carbonates and hydroxides

Compound	pKs*	Compound	pKs
$CaCO_3$	8.3	$Ca(OH)_2$	5.2
$NiCO_3$	8.2	$Ni(OH)_2$	15.2
$BaCO_3$	8.3	$Ba(OH)_2$	3.6
$SrCO_3$	9.0	$Sr(OH)_2$	3.9
$ZnCO_3$	9.1	$Zn(OH)_2$	16.0
$CuCO_3$	9.9	$Cu(OH)_2$	19.3
$MnCO_3$	9.3	$Mn(OH)_2$	12.8
$CoCO_3$	10.0	$Co(OH)_2$	14.9
Ag_2CO_3	11.1	$Ag_2(OH)_2$	7.7
$FeCO_3$	10.7	$Fe(OH)_2$	15.1
$PbCO_3$	13.5	$Pb(OH)_2$	15.0
$CdCO_3$	13.7	$Cd(OH)_2$	14.4
$HgCO_3$	16.0	$Hg(OH)_2$	23.7

*pKs – negative logarithm of solubility product.

The selected system of recirculation of a carbonate solution over the reactor and the sand filter proved to be reliable and robust. In general, the efficiency can be raised by selecting a rather high pH due to applying a high recycle ratio.

The following conclusions can be drawn:

1. In treating spent Zn-baths, hardly any amorphous matter is formed, so that the sand filter is probably superfluous. The process efficiency is high and can be influenced by the pH. At a pH of 8.5–9, very low effluent concentrations can be achieved (a few milligrams per litre).

2. In treating spent Ni-baths, amorphous matter always occurs, so that a sand filter is necessary to increase the efficiency. As known, the backwash water from the sand filter can be returned to the acid bath, where the amorphous matter dissolves again and can be removed in the following cycle in the pellet reactor.

In treating Cu-solutions and applying a high recycle ratio, very high efficiencies can be achieved. No amorphous matter is formed and the effluent concentration is below 2 ppm.

5. REUSE OF PELLETS

Pellet analyses show that the Zn- and Ni-pellets contain respectively more then 99.7% Zn (rest: Fe, Cr) and 99.8% Ni (rest: Fe). The pellets can be considered as being quite pure. The Zn-pellets contain 70–95% carbonate and small quantities of other ligands (mainly OH^-). The Ni-pellets contain 50–60% carbonate and large quantities of other ligands (mainly OH^-). The composition of the copper pellets corresponds very well to that of malachite.

The pellets can be reused in the metal industries, e.g., to prepare concentrate baths by dissolution of the metal with chloric or sulfuric acid. This has been confirmed by applying a Hulcell test on concentrate baths prepared from pellets.

6. APPLICATION IN PRACTICE

Experience in drinking water and wastewater treatment provides a good basis for the application of pellet reactors in practice. It may also be remarked that scaling up is hardly necessary as the capacity, of the pilot-plants is sufficient to treat the wastewater flow from a 1 m^3 bath in a few hours.

Due to the diversity of the electro-plating industry, application in practice will have to be worked out in further detail. Major aspects of optimization for each plant concerned will be:

Selection of optimal working conditions (pH, C_T, pellet size).
Engineering.
Reuse of pellets.

7. COSTS

Investments costs:
- including filter,
- fully automatic.

Reactor diameter (cm)	Hydraulic capacity (m^3/h)	Investment costs (US $)
10	0.3–0.8	20,000
20	1.2–3	35,000
40	5–12.5	50,000
80	20–50	80,000

Operational costs:
- 1 hour attendance a day,
- chemicals: 500–700 US $/ton metal.

Savings:
- purchase of heavy metal: 1,000–30,000 US $/ton metal,
- disposal of chemical waste: 350–2,000 US $/ton metal (disposal costs 130 US $/ton chemical waste).

The investment costs are relatively small, being anticipated at US \$ 20,000 to 35,000 for plants of 0.5 to 4 m^3/h. Operational costs consist mainly of the cost of chemicals, estimated at US \$ 500–700 per ton metal. Against these costs the savings on the purchase of heavy metals can be considerable. At a bath concentration of 5 g/dm^3 and a metal price of US \$ 10 per kg, these savings amount to US \$ 50 per m^3. Furthermore, there will be lower costs for the operation of the hydroxide precipitation unit (chemicals) and the disposal of hydroxide sludge. The last item greatly depends on local circumstances, but is generally very considerable (approx. US \$ 130 per ton of sludge).