

The Reduction of Zinc using Goethite Process and Adsorption of Pb^{+II} , Cu^{+II} and Cr^{+III} on Selected Precipitate

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Abstract— This paper deals with the problem of waste sludge from the production of zinc chloride in the company Bochemie. This sludge contains a high degree of zinc (therefore it cannot be used to charge a blast furnace) and a significant amount of dangerous waste is created. Waste sludge was treated under laboratory conditions, using the goethite precipitation process. Selected ferro-precipitate was used as immobilization agent for removing heavy metals from aqueous solutions. Lead, copper and chromium were used as model metals. The simultaneous measurements of the heavy metals adsorption and zeta potential determination of the (adsorption) suspensions were carried out. The adsorption isotherms were found to be of typical Langmuir type; values of the heavy metals adsorption capacities have been calculated ($a_m = 0.76$ mmol/ g for lead, 0.58 mmol/g for copper, 0.38 mmol/ g for chromium, respectively). Shape of the adsorption isotherms was correlated with zeta potential values at the adsorption equilibrium. Addition of the heavy metals ions affects the value of ξ - potential, making the zeta potential values more positive.

Index Terms— adsorption, ferro-precipitate, goethite process, heavy metals, zeta potential

I. INTRODUCTION

In the company Bochemie, zinc chloride is manufactured particularly from recycled acid, which represents waste from zinc works. At first, the solution is neutralized by zinc ashes. The next step is eliminating iron from the solution by means of precipitation. The solution contains ferrous ions which oxidize to form ferric ions. The simultaneous precipitation of iron is carried out in melting boilers where the pH of the solution is adjusted to approximately 3 – 3.5, and hydrogen peroxide is added at such speed that the solution would not foam out of the boiler. Thus, most of the iron is precipitated and the pH of the solution decreases (unless sufficient surplus zinc ashes or other solid waste are put in). This suspension is pumped over into a refining boiler; the solution is heated to approximately 50°C and subsequently to 80 °C to decompose surplus peroxide. pH and red-ox potential are continuously checked and adjusted. Finally, the suspension is filtered and the clear solution is further cemented by zinc ashes which

eliminate heavy metals. This way, the solution has been cleared. The final product is the result of evaporating the solution in a vacuum evaporator.

The problem of the above described production is the thick and almost unsettling sediment of iron which, moreover, retains rather big amounts of zinc chloride. The sludge consists of approximately one third of water, one third of zinc chloride and the rest are ferro-compounds. Due to the presence of zinc chloride, the sludge cannot be used to charge a blast furnace. Approximately 200 – 300 tons of this sludge are taken to the dump annually. The increasing charges for dumping the sludge and the fact that it contains almost 70 tons of zinc chloride have a negative impact on the economy of producing zinc chloride in Bochemie. The solution is to find a suitable process of precipitating iron in solutions, e.g. using the goethite process.

The goethite process is successfully used in the electrolytic galvanization industry to turn the iron in a solution (mostly sulfide or chloride) into a sediment which is easy to filtrate. [1], [2] The Electrolytic Zinc Company of Australasia developed a continuous process, during which all ferrous ions in a solution are at first oxidized, and subsequently the solution continuously flows into a reactor at a speed which eliminates the solid phase. [3]

This method was also used to precipitate iron from the waste acid used to produce zinc chloride in the company Bochemie. The process was carried out under varied conditions (time, temperature, pH) and resulted in sediments with varied composition and texture parameters. Sediments high in zinc, further use of which is rather limited, were analyzed with regard to their possible use as sorbents to eliminate heavy metals from aqueous solutions.

Heavy metals in waste water cause a serious environmental problem. Recently, efforts have occurred to eliminate the content of heavy metals by means of adsorption on various types of adsorption materials. Apart from the most common active coal, also cheaper options are analyzed. The following natural materials are used – various kinds of coal (lignite coals, charcoal, brown coal, bituminous coal), humic acids, peat, algae, woolen or rice materials. [4]-[8] The second category are waste materials, e.g. various kinds of sludge. Other interesting adsorbents offering good prospects are as well ferro-compounds such as goethite, hematite, magnetite and others. [9]-[13] These compounds are very often artificially synthesized and used as nano-adsorbents. These oxi ferro-compounds as well arise as waste products in particular manufacturing processes, e.g.

Another aim of this study is to judge waste materials on the basis of ferrous oxide as adsorption material to eliminate ions of selected heavy metals from solutions. Further goals were

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to describe the adsorption process by means of some adsorption theory (Langmuir, Freundlich) and to calculate the adsorption capacity of the sorbent. By means of the zeta potential, changes on the surface of adsorption particles were monitored during the adsorption process.

II. EXPERIMENTAL METHODS

A. The VM Goethite Process

This process introduced by the company Vieille Montagne (hereafter only the VM process) is based on reducing all the iron in a solution to bivalent iron and subsequently slowly oxidizing it by the air or another oxidizing agent, while maintaining the basic concentration criterion. This process is carried out in a discontinuous reactor. An apparatus was designed and created and it was used to carry out the VM goethite precipitation under conditions that are described as optimum in this article. Approximately 1,000 ml of recycled acid was poured into a reaction vessel (a 2,000 ml beaker). Large impurities had been removed from the acid by means of filtrating it over a textile filter. The discharge of the 3 % hydrogen peroxide was set on a peristaltic pump according to the length of the experiment (2 hours 2.6 ml.min⁻¹ or 4 hours 1.3 ml.min⁻¹). A pH electrode, a stirrer and hoses from both pumps (with hydrogen peroxide and a zinc oxide suspension) were immersed into the reaction vessel. The stirrer was switched on and pH was adjusted to the desired level (by manually adding the zinc oxide suspension). After having reached the desired temperature 80 °C and pH, both pumps and a computer program for pH were switched on. This way, the experiment began. After two or four hours (τ), an approximately 50 ml sample was taken from the reactor. The sample was filtrated and a little hydrogen peroxide was added into the filtrate until its color changed (i.e. all ferrous ions have oxidized into ferric ions). At this stage, the experiment was stopped.

The samples were named according to the conditions, under which they were created: VM254 (pH = 2.5 and τ = 4 h), VM252 (pH = 2.5 and τ = 2 h), VM304 (pH = 3.0 and τ = 4 h), VM302 (pH = 3.0 and τ = 2 h). Higher pH could not be achieved under standard conditions. One more precipitation called VM254B was carried out under the same conditions as VM254 with one difference – ferric ions had been removed from the filtrated leach liquor. The last experiment VM254X was carried out to determine the impact of the leach liquor (another batch) on precipitation. The speed of filtration of all samples was measured and calculated. The content of iron in the filtrate and zinc, iron and chlorides in the sediment were also determined.

B. The EZ Goethite Process

The Electrolytic Zinc Company of Australasia developed a continuous process, during which all ferrous ions in a solution are at first oxidized, and subsequently the solution continuously flows into a reactor at a speed which eliminates the solid phase. Therefore, a continuous flow reactor is used in this process. The apparatus for this process was designed and created similarly to the VM process. 800 g of zinc chloride solution was put into a reaction vessel (filtering

flask). The solution had been prepared by dissolving 240 g of solid zinc chloride in 560 g of distilled water. Recycled acid was rid of solid impurities by filtering it over a textile filter. Subsequently, all ferrous ions were oxidized into ferric ions by slowly adding hydrogen peroxide (30 %) and continuously stirring the substance. Occasional checks were carried out to find out whether all the iron had oxidized. The discharge of oxidized acid into the reaction vessel was set on a peristaltic pump (a 2-hour experiment – 8.4 ml.min⁻¹, or 4 hours 4.2 ml.min⁻¹). A pH electrode, a stirrer and hoses from both pumps (with oxidized recycled acid and a zinc oxide suspension) were immersed into the reaction vessel. The stirrer was switched on. After having reached the desired temperature 80 °C and pH, both pumps and a computer program for pH were switched on. This way, the experiment began. The experiment finished after two or four hours.

The samples were named after conditions: EZ254 (pH = 2.5 and τ = 4 h), EZ252 (pH = 2.5 and τ = 2 h), EZ304 (pH = 3.0 and τ = 4 h), EZ302 (pH = 3.0 and τ = 2 h), EZ354 (pH = 3.5 and τ = 4 h), EZ352 (pH = 3.5 and τ = 4 h). Another precipitation named EZ254X was carried out to test whether the fact that the recycled acid comes from a different batch influences the process. The speed of filtration of all samples was measured and calculated. The content of iron in the filtrate and zinc, iron and chlorides in the sediment were also determined.

C. Air oxidation

If the current oxidizing agent (hydrogen peroxide) was substituted by air oxygen, the whole production would result in considerable savings. This experiment was based on the work of three students done in the company Lachema Bohumín between 1984 and 1985. Their paper included not only a sketch of the apparatus but also the conditions under which total oxidation of ferrous ions takes place: 0.945 g.dm⁻³ of a catalytic agent in the form of copper chloride, minimum temperature of the solution = 60 °C (higher temperature is irrelevant), minimum flow of air = 0.6 dm³.min⁻¹ related to 1.5 dm³, and minimum running speed 600 turns per minute. The experiment was carried out using a model sample (capacity 1.5 dm³, 13 – 15 g.dm⁻³ of ferrous ions and 650 – 720 g.dm⁻³ of zinc chloride).

1,200 ml of recycled acid was put into a sulphonation flask. The acid had been rid of large impurities by filtrating it over a textile filter, and approximately 1.314 g of copper chloride had been added. An air input from an air pump, a stirrer and an inlet of the zinc chloride suspension were inserted into the main neck of the reaction vessel. The second neck was fitted with a cooler, the third one with a pH electrode and the last one with a thermometer. The whole apparatus was closed hermetically; air could escape only through the cooler. The stirrer was switched on and pH adjusted to the desired level. After having reached the desired temperature and pH, the pump, the air pump and a computer program for pH were switched on. This way, the experiment began.

After four hours, an approximately 50 ml-sample was taken from the reactor. The sample was filtered, creating a yellowish filtrate. The experiment was carried out also for longer time (maximum 6 hours); however, total oxidation of ferrous ions never occurred. To determine the extent of

oxidation, the experiment was carried out two more times, namely for pH 2.5 and 3.0. Gradually, samples were taken before the beginning of oxidation and then after 15, 45, 105, 225 and approximately 240 minutes (i.e. after the end of the experiment). A 50 ml-sample was taken by a pipette and filtered over a regular filter and a funnel.

The content of iron in the individual samples was determined. In the two experiments, the speed of filtration was measured and calculated and the content of zinc, iron and chlorides in the sediment was determined.

Real samples were used in the lab. Goethite precipitation as well as air oxidation were carried out directly in the lab of the company Bochemie a.s., using recycled acid. As this acid represents waste from zinc works, its composition varies. The solution contains between 30 and 40 % of zinc (sometimes even more), 1 – 1.5 % of iron mostly in the form of ferrous ions, and traces of lead, cadmium, copper, sodium, potassium and calcium. The main part of the solution is taken up by water.

In all experiments, pure zinc oxide was used to adjust (increase) pH. 30% hydrogen peroxide diluted to 3 % distilled water was used. Before the beginning of the experiment, a 30 % solution of zinc chloride (240 g of zinc chloride (s) + 560 g of distilled water) was added to the reaction vessel. The catalytic agent for air oxidation was copper chloride (s).

D. Adsorbent-VM254

Out of number of precipitates has been selected one sample with rather high content of zinc. The content of iron and zinc in the sediment created by the above mentioned process was determined. Surface area (BET) was as well determined and the sample was observed by RTG diffraction. Results are summarized in table 1.

TABLE I PROXIMATE ANALYSES, SURFACE AREA AND MINERAL COMPOSITION

Fe	Zn	S ^{BET}	RTG diffraction
%	%	m ² /g	
47.5	7.0	220.5	ferrihydrite + ferrosyhyte

The surface area of the sample from the adsorption isotherms of nitrogen (SBET) was evaluated according to BET theory, using a nitrogen molecular area of 0.162 nm² for the calculation.

The normal powder XRD patterns were recorded between 5.0° and 50.0° 2 θ using CuKα1 radiation with an INEL CPS 120 diffractometer equipped with a curved position-sensitive detector, in transmission mode with a germanium monochromator.

E. Chemicals

The chemical used in this study was zinc chloride, zinc oxide, copper chloride, hydrogen peroxide, lead nitrate, copper nitrate and chromium nitrate. All the solutions were made in distilled water. Analytical grade chemicals were used.

F. Batch Experiments

About 0.2 g of dried sample was added to 50 mL of a given metal solutions of known concentration varying in the range 10 - 0.1 mmol/l and occasionally shaken. Adsorption

equilibration took about 3 days, as deduced from previous measurements. The zeta potential of the adsorption suspensions was measured. Then, the sample was removed by filtering through paper filter. The metal concentration of the filtered solutions was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The amount of metal adsorbed (a) was determined from the change in the solution concentration before and after equilibrium, according to:

$$a = \frac{(c_0 - c_e)V}{m} \quad (1)$$

where c_0 is the initial concentration of metal solution, c_e the concentration of metal solution at the adsorption equilibrium, V the volume of metal solution and m the mass of the sample.

G. Zeta Potential Measurements

Zeta potential measurements was performed by analyzing 0.2 g of coal in 50 ml metal solution using the Coulter Delsa 440 SX (Coulter Electronic, USA). Delsa 440 SX uses the scattering effect of Doppler light to determine the electrophoretic mobility. The zeta potential was obtained from the electrophoretic mobility by the Smoluchowski equation:

$$\zeta = \frac{\mu \cdot \eta}{\epsilon} \quad (2)$$

ζ is the zeta potential (V), η represents dynamic viscosity (Pa.s), and ϵ stands for the dielectric constant. The fixed conditions of measuring were the following ones: temperature (298 K), electric field (15 V), frequency (500 Hz), and the properties of the samples – viscosity (0.0089 kg/m.s), refraction index (1.333), and dielectric constant (78.36).

III. RESULTS AND DISCUSSION

A. Goethite process

The VM experiments in the discontinuous reactor proved that the optimum pH was 2.5. With a higher pH, the sediment was almost impossible to filtrate. Reducing the reaction time from four to two hours did not bring positive results either. The content of iron in the filtrate was almost the same in all samples, ranging between 0 and 1 ppm (2 ppm in one sample), which represents an insignificant amount and does not have any impact on the quality of the product. However, the composition of the sediment differed more significantly. The smallest proportion of zinc was in sediments created by experiments with pH 2.5 and reaction time four hours. The concentration of zinc in such sediments was between 6.4 and 7.0 wt %, which represents a significant decrease in comparison with the current sludge containing approximately one third of zinc chloride. The content of zinc in the sediment in the other experiments was over 25 wt %.

If the speed of the VM254 sample (the input raw material was filtered recycled acid) and of the VM254B sample (the input raw material was filtered recycled acid after reducing all ferric ions) are compared, it is evident that the speed of filtration of the VM254B sample is higher, which corresponds to the information gained from the article.

Reducing all ions to their ferrous form is not very easy; a cheap reducing agent, which would not pollute the final product zinc chloride, is difficult to find. The speed of filtration differed by approximately $30 \text{ ml.mm.min}^{-1}$, which does not represent a big difference and is insignificant with respect to the demands of the reduction. The VM254X sample shows that if the experiment is carried out with different recycled acid, the speed of filtration is comparable.

The EZ experiments in the continuous reactor proved that the filtration of the sediment was the fastest in the EZ254 experiment, i.e. under the same conditions as in the VM process. The speed of filtration of the EZ254 sample significantly differed from the other samples ($1061.5 \text{ ml.mm.min}^{-1}$). Comparing the speed of the EZ and the VM processes, it is evident that the filtration of the sediment is generally faster in the EZ process. The content of iron in the filtrate was almost the same in all samples, ranging between 0 and 1 ppm, which represents an insignificant amount and does not have any impact on the quality of the product. However, the composition of the sediment differed more significantly. The smallest proportion of zinc was in sediments created by experiments with pH 2.5 and 3, and the effect of the reaction time is practically minimum. The concentration of zinc in such sediments was between 1.4 and 4.5 wt %, which is less than in the VM process. In experiments with pH 3.5, the content of zinc in the sediment was over 30 %. This proportion is probably caused by the fact that to reach such a high pH, a large amount of the zinc chloride suspension has to be added into the reacting compound during precipitation.

The EZ254X sample shows that, even though the experiment was carried out under the same conditions as EZ254, the speed of filtration differed significantly due to using recycled acid from another batch. It can be said that the quality of the sediment depends on the recycled acid which is used as raw material, as the experiments EZ254, EZ302 and EZ304, whose speed of filtration differed significantly, were carried out from recycled acid taken on the same day. Comparing the speed of filtration of the VM254X and the EZ254X experiments, in which the same recycled acid was used, it once again has to be established that better results were achieved by the EZ process. Apart from the fact that the speed of filtration is higher, the content of iron in the filtrate is lower and the sediment contains less zinc.

Other experiments tested whether air oxygen could not be used as an oxidizing agent instead of hydrogen peroxide. These experiments were carried out with pH 2.5 a 3.0 (OV25 and OV3) and the minimum time of precipitation was four hours. Unfortunately, total oxidation and precipitation of iron never occurred. During precipitation, at least samples were taken and the content of iron was subsequently determined. Even though the content of iron was decreasing, oxidation was not fast enough to be implemented into operation. The reaction works better with higher pH, which corresponds to the project the experiment was based upon. If pH was increased, total oxidation and precipitation might occur already after four hours, however, at the expense of a high content of zinc in the sediment, like in the EZ and VM experiments. All results are reported in table 2.

TABLE II GENERAL OVERVIEW OF OUTCOMES

Conditions	pH	τ [h]	Speed of filtration [ml.mm. min ⁻¹]	Soluti on analysi s			
				Fe [ppm]	Zn [%wt .]	Fe [%wt .]	Cl ⁻ [%wt .]
EZ252	2.5	2	147.3	1	1.5	48.0	3.7
EZ254	2.5	4	1061.5	1	1.4	54.0	1.2
EZ302	3.0	2	205.0	1	4.5	55.5	1.2
EZ304	3.0	4	492.9	1	4.2	53.5	4.0
EZ352	3.5	2	100.9	0	31.9	20.5	20.4
EZ354	3.5	4	58.1	1	30.1	25.5	19.4
EZ254X	2.5	4	133.9	0	4.5	48.5	2.5
VM252	2.5	2	28.8	0	9.9	47.0	3.7
VM254	2.5	4	105.6	0	7.0	47.5	1.2
VM254B	2.5	4	135.2	1	6.4	45.0	3.1
VM302	3.0	2	51.3	0	27.6	29.0	15.2
VM304	3.0	4	43.3	1	25.2	31.0	12.1
VM254X	2.5	4	105.8	2	6.5	48.0	2.1
OV3	3.0	4	41.0	-	13.0	39.5	8.1
OV25	2.5	4	57.7	-	11.8	41.0	6.8

B. Characterization of Sample

Data from RTG diffraction show that the sample contains a significant amount of amorphous phase; the following two ferrous compounds are present - ferrihydrite $\text{Fe}_5\text{O}_7(\text{OH}) \cdot 4\text{H}_2\text{O}$ (30%) and ferroxihite $\delta\text{-FeO}(\text{OH})$ (20%). The relatively high content of zinc makes disposal of this material (waste) in blast furnace impossible. This fact represents the main reason for looking for new (other) effective ways of using this material. The relatively large specific surface area contributes to using the material as adsorbent (see table 1).

C. Adsorption of Metallic Ions

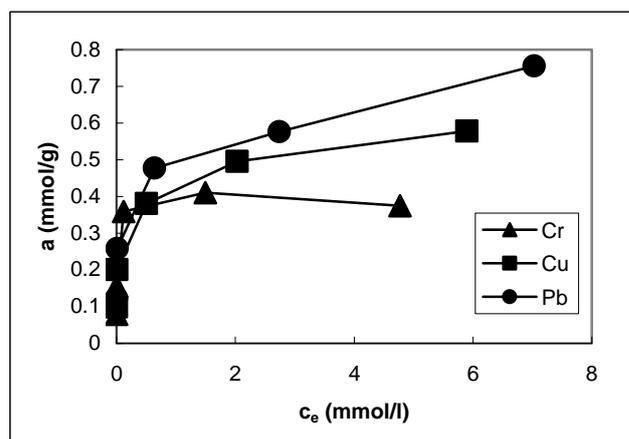


Fig 1. Adsorption of Pb, Cu and Cr ions on ferro-precipitate

Figure 1 depicts typical adsorption isotherms obtained from the experimental data. The shape of isotherms indicates that the adsorption data could be well fitted by the Langmuir adsorption model of monolayer coverage. In a linear form, the Langmuir equation is given by

$$\frac{c_e}{a} = \frac{c_e}{a_m} + \frac{1}{a_m b} \quad (3)$$

where a is the amount of the metallic ion adsorbed, c_e is an

equilibrium concentration of the metallic ion in solution, b represents a monolayer binding constant and a_m is the monolayer adsorption capacity.

All adsorption isotherms proved to be consistent with the Langmuir model as deduced from calculated r-square values close to 1 (minimal r^2 value was 0.985). The most informative parameter in the Langmuir equation is a_m , providing information on adsorbed amount at monolayer surface coverage. These values are compiled in Table 2 as found for studied samples.

From the Table 2 it is obvious that Pb^{2+} cation is immobilized in the largest extent, opposite, Cr^{3+} cation is of the lowest affinity to the sample.

TABLE III RESULTS OBTAINED FROM THE LANGMUIR EQUATION APPLIED TO THE ADSORPTION DATA

Langmuir isotherm			
Ion	a_m (mmol/g)	b (l/mmol)	r^2
Pb	0.756	4.001	0.985
Cu	0.584	7.112	0.996
Cr	0.376	46.296	0.999

The Langmuir adsorption theory is based on adsorption of gases and it is not apparently valid without any differences for adsorption from the solutions. Thus, the experimentally obtained data were also analyzed in terms of non-linear regression. Four adsorption models (Langmuir, Freundlich, Langmuir-Freundlich and Temkin) were used and compared. The non-linear regression was calculated by means of OPstat program using various algorithms – genetic algorithm, simplex, and Levenberg-Marquardt algorithm. Akaike criterion was chosen to evaluate the experimental data correspondence with a given theory. The lowest value of Akaike criterion was found for Langmuir model. In other words also non-linear regression confirmed Langmuir model applicability.

D. Zeta Potential Measurements

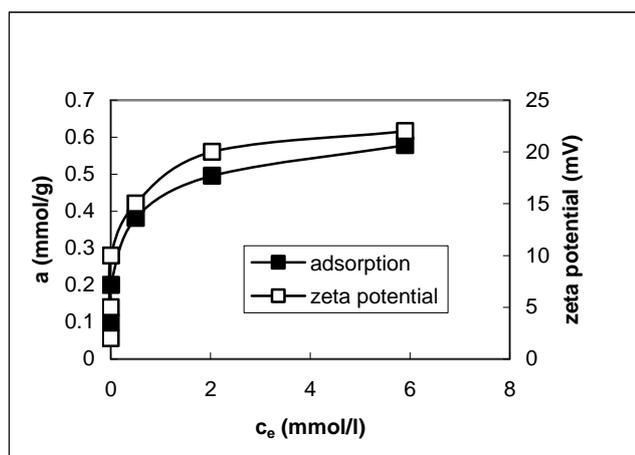


Fig. 2: Dependence of zeta potential (blank symbols) and adsorption of Cu (full symbols) on ferro-precipitate on the equilibrium concentration of the Cu solution (c_e).

Figure 2 shows the noteworthy similarity of the adsorption isotherms with the changes of zeta potential of the adsorption systems. In other words the adsorption of metal ions causes a

change of the surface charge. The same results were found for other adsorption systems. [14]- [17].

IV. CONCLUSIONS

The VM and EZ processes have proved that the ideal conditions are pH 2.5 and reaction time approximately four hours. In comparison with the current sludge, the content of zinc in the sediment has been significantly reduced. The EZ process showed better results. The results as well prove that recycled acid can significantly influence the whole precipitation. Therefore, it is necessary to make sure that the composition of the acid in the individual batches does not differ much.

The outcomes of the experiments prove that the EZ process is more suitable to be implemented. However, rebuilding the premises would be more expensive than converting the operation into using the discontinuous reactor (VM). Therefore, the optimum solution is to test both methods in pilot plant, namely under the already mentioned conditions (pH 2.5, reaction time minimum four hours and temperature 80 °C). Moreover, all experiments should be carried out using the same recycled acid. Sediments produced in pilot plant should be analyzed using RTG diffraction and thermal analysis to determine their composition and the way the sediment reacts to higher temperatures. After comparing the outcomes of the analyses, it is recommended to complete a review showing whether the potential lower speed of filtration in the VM process is more acceptable than the more expensive rebuilding of the premises for the continuous reactor (EZ). Production can be as well inhibited by the vacuum evaporator which represents the final element in the production of zinc chloride. Therefore, it is possible that the speed of filtration of the sediment created by the VM process will be sufficient.

To get sediment which is easy to filtrate and contains only little zinc, the premises of the factory will have to be automated. Similarly to experiments carried out in a laboratory, pH will have to be controlled by computers. All constituents must be measured out accurately by pumps or automatic batch meters.

Adsorption of selected ions of heavy metals on sediment was monitored. Apart from the amorphous phase, the sediment contained also ferrihydrite and ferroxhite. This material, which represents unusable waste, shows a relatively high adsorption capacity for heavy metal ions. The adsorption process can be described by the “classic” Langmuir theory and the calculated parameters of the Langmuir equation can be used for potential particular applications. The adsorption process was studied as well with regard to changes of surface charge. Measuring proved a connection between adsorption and the change of the zeta potential of the particles. Particularly due to its adsorption capacity and price, this material ranks among many cheap adsorption materials possibly usable to treat waste water containing heavy metals.

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