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Research Article

Treatment of contaminated water in the zinc unit in the Trepça complex

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Abstract:

One of the biggest sources of pollution land and water are industrial waste waters. At section of zinc industry in complex Trepca during the process of zinc production are gained wastewater where their negative impact is wider extent of contamination of land with which it comes in contact and in this case comes to the accumulation ions of heavy metals, surface- water and then mixing with groundwater and pollution. Directly with vulnerable is Sitnica river, in which contaminated water flows from the industrial unit for the production of Zn, which flows into the Iber river, which still flows into the Morava river in Serbia, thus presents a problem internationally. The objective of the paper is concerned with the characteristics of industrial wastewater from the section of zinc in Trepca complex and their impact on water pollution around. Are made quantitative and qualitative analyses of samples of polluted water before and after the production process and is found high content of ions of heavy metals such as: Pb, Zn, Cu, Fe, Cd, Bi, Ni, Co, Sb, Sn, etc., and which exceed the values of MLD, provided by international legislative rules. Neutralization is made of industrial wastewater based on the pH value and concluded that the water is rich belongs to the category of IV water according to legal regulations for water.

1. Introduction

Natural water is clean and basic and indispensable element for human life, plant and animals, so is the principle that all the inhabitants of the planet to care for the exploitation and protection of his right. Population growth and rapid development of society in terms of technological industry and has lead to enormous exploitation of water resources as well as to excessive pollution of water (surface-and groundwater).In recent decades, as locally and internationaly importance that special attention is paid to cleaning of industrial wastewater, in order to improve the level of water pollution [1,2]. A special emphasis is paid of equipment, automation for the processing of wastewater with dosing reagent then high frequency of cleaning of metal ions with slaked limes, eligibility and elements present in the molten. Water that is used in technological processes for the production of metal is actually contaminated water. The degree of contamination depends on the amount of waste that water contains. While matter pollutants coming from industrial units, then it comes to industrial wastewater, while if they come from more than urban households having then it comes to municipal wastewater [3]. So that these waters back in kind and used again they must undergo purification process, which is performed through mechanical methods, chemical and biological. Chemical methods for purification of water mean water purification process, which is based on chemical reactions and physic-chemical phenomena. Chemical process for the purification of water is very costly, but for cleaning the impurities present in the water some chemical process is no alternative. As a base chemical cleaning process of polluted water from some solvable matteries is: With chemical precipitation with ion exchange, gas blow oxidation and adsorption. Industrial wastewater resulting from the different sections of the technological processes, but as their common characteristic is the high degree of toxicity receptors.

The toxicity of these waste water is expressed by the degree of acidity and alkaline in the presence of a number of heavy metals, phenols, mineral oils and detergents [4,5].

2. Material and Methods

Equipment for processing of industrial wastewater with neutralization process are intended for: receiving, neutralization and water purification, as well as filtering waste from contaminated water. Liquid waste which come from different sections collected in the basin 93 VE 93 16. One of pumps PP 18 A / B made pumping in tank for neutralization in 93 VE 18 A / B that are located at cascade mood Slaked lime obtained from the processing of quick lime, which is transported through track and is stored in the bunker 93 BN 10. And slaked lime through extractor 93 CV 11, with the help of pneumatic valve, drawn and with spiral transporters 93 CV 12 forwards so booked for the preparation milk lime, where the reservoir is equipped with agitator 93 VE 13. Measurer level, through the contactor with the upper and lower part, made the opening for the supply of lime and water when the lower level is reached and interrupt when the upper level is reached. Preparing thus becomes the lime with 10% $Ca(OH)_2$. Specific weight of hydrated lime optimal adjusted based on experience. The injection of lime made in two reservoirs, so that neutralization is done in stages, at pH 4-5 in the reservoir 93 VE 18 and at pH= 7 in the reservoir 93 VE 18 B. The third reservoir for flotation 93 V 20 also is placed in cascade mode compared with the reservoir93VE18A/B. Reagent for flokulim, $FeClSO_4$, preparation mechanically with 10% to rezervoir 93 VE 22 andwith the aid pump for dosing PP 93 24 A / B, the flow of which is regulated mechanically and sent to the reservoir 93 VE 20. In cases where the pH value measured in the reservoir 93 V 18 B is low, then through a tube contaminated water turn in the basin 93 VE 16 through automatic valve which is located at the outlet of the reservoir 93 VE 20. The solution whose is added flocculant (layer) through gravity sent to precipitation 93 TN 29. We added at supplier cylinder of precipitator polyelectrolyte which serves as a catalyst for precipitation. This polyelectrolyte preparation mechanically by 0.1% in the reservoir 93 VE 26 and injected through a dosing pump PP 93 28 A/B, where the flow is regulated mechanically. The clean neutralized solution flow from precipitator with gravitation and goes to the river. Precipitate collected at the end of precipator passes through the reservoir to homogenise 93 VE 31, and with the help of a membrane pump PP 93 32 A / B pumped into the filtration equipment. Obtained precipitate undergoing processing, while filtrate goes into the river. The report between pH values and the amount of lead, zinc and cadmium in the treatment of wastewater with lime water is presented at figure 1.

3. Results and Discussions

The degree of efficiency during precipitation of heavy metals depending on the pH value of industrial waste water processing of zinc metallurgy Practically is confirmed that the process of cleaning wastewater with slaked lime in the form suspension is economical. The reason of process to processing with slaked lime based in the fact that most metal ions precipitate in the form of hydroxides, where the rate of precipitation, where them precipitation scale depends how like the homogeneity, concentration of metal ions and the amount of dosed of lime that depends on the pH value. The process of neutralization of acidic wastewater is carried out in pH = 7.5-8.5, which in this case comes to heavy metal precipitation.

As a result of the neutralization process and hydrolysis acidic wastewater that comes to precipitation of heavy metals in the form of hydroxide, but as a result of the presence of calcium carbonate comes even to the formation of carbonate. With the introduction of chemical reagent made destabilization of colloids as a result of this we have the process of coagulation. Giving the reagents, which ions react with colloids comes to the elimination of electrostatic forces in colloids.

As a result of the coagulation process and the formation of more fluxes, to which precipitate. With this reach the precipitation of heavy metals from wastewater, regardless of pH values for some oxides, such as are given in table 1.

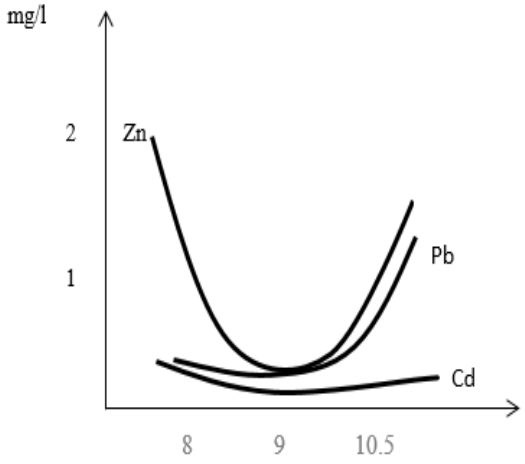

Figure 1. *The report between pH values and the amount of lead, zinc and cadmium in the treatment of wastewater with lime water.*

Table 1. *precipitation of pH values of some heavy metal hydroxides are as follows:*

Hydroxide	pH value
$Pb(OH)_2$	6
$Zn(OH)_2$	6
$Mg(OH)_2$	11
AgOH	9
$Hg(OH)_2$	7-8
$Ca(OH)_2$	7-8
$Cu(OH)_2$	6
$Cd(OH)_2$	7-8
$Zr(OH)_2$	4
$Fe(OH)_3$	2-3
$Ge(OH)_4$	2-3
$Ti(OH)_3$	4
$Ni(OH)_2$	7-8
$Pb(OH)_4$	7-8
$Bi(OH)_3$	6
$Al(OH)_3$	4

Also process wastewater processing is done with the help of flocculant and polyelectrolyte.

$FeClSO_4$ is used as an electrolyte, which serves to create greater floske. Thus the reaction between H_2SO_4 and $Ca(OH)_2$ occurs the formation of $CaSO_4$, which is characterized by product solubility lower, which runs the precipitate and detached attracts the heavy metals in the form of hydroxide, as follow reactions:

$ZnSO_4 + Ca(OH)_2 + 2H_2O = Zn(OH)_2 + CaSO_4 + 2H_2O$

$CdSO_4 + Ca(OH)_2 + 2H2O = Cd(OH)_2 + CaSO_4 + 2H_2O$ $2PbCO_3 + Pb(OH)_2 = 2\ Pb\ CO_3 \times Pb(OH)_2$

$PbSO_4 + Ca(OH)_2 + H_2O \cdot CO_2 = PbCO_3 + CaSO_4 + H_2O$

$Pb^{2+} + Ca(OH)_2 = Pb(OH)_2 + Ca^{++}$

$H_2SO_4 + Ca(OH)_2 + 2\ H_2O = CaSO_4 + 4H_2O$

$CuSO_4 + Ca(OH)_2 = Cu(OH)_2 + CaSO_4$

Verification scale of precipitation of heavy metals and neutralization complete with chalk erased depending on the pH is made independently of content, Pb, Zn, Cu and Cd and that both before and after cleaning the wastewater industrial.

It also has become the research content of heavy metals even in certain pH values of 9 to 10.5 in reservoirs for wastewater neutralization.

Analysis for heavy metals are carried out polarigraphic method and results are given in the table. Wastewater samples were taken every 2 hours and it shaped composite.

The wastewater that enters in the object for treatment is characterized by high acidity and a high content of base metals. Based on the selected technology, the facility is dimensioned to accept the maximum loads that can occur in the installation.

For this purpose, two research methods have been chosen:

- To estimate the average load values, when dealing with normal production and
- With maximum loads according to the given technological schemes

Table 2.*Sample no. 1.*

Sample 1 (mg /l)					
Wastewater	pH	Pb	Zn	Cu	Cd
Before cleaning	2.5	3.8	985	1.6	2.7
After cleaning	8	2.3	350	1.1	1.3
After cleaning	9	1.1	130	0.23	0.3
After cleaning	10.5	0.45	11.5	T	T
The eficasity scale of cleaning		88.15	98.83	99.99	99.99

Table 3*.Sample nr.2.*

Sample 2 (mg /l)					
Wastewater	pH	Pb	Zn	Cu	Cd
Para pastrimit Before cleaning	1.9	0.9	904	2.6	1.7
Pas pastrimit After cleaning	8	0.5	305	1.4	1.2
Pas pastrimit After cleaning	9	0.24	110	0.78	0.6
Pas pastrimit After cleaning	10.5	0.12	23.3	0.34	0.15
The eficasity scale of cleaning		86.66	97.42	86.92	91.17

Table 4.*Sample nr.3.*

Mostra 3 (mg /l)					
Wastewater	pH	Pb	Zn	Cu	Cd
Before cleaning	1.5	1.9	1250	1.34	2.7
After cleaning	8	0.4	340	0.7	0.23
After cleaning	9	0.5	85	T	T
After cleaning	10.5	0.03	9.6	T	T
The eficasity scale of cleaning		98.42	99.23	99.99	99.99

According to the tab. data and diagrams, it is observed that the efficient sedimentation of heavy metals begins after pH values of 8, so that each metal is characterized by the range of pH values at which its depletion begins.However, the general conclusion not only from process researchers, but also from professionals for the protection of the working environment and the promotion of the environment in the wider range is that the efficient sedimentation of metals is at pH values of 9-10.2, which are the most favourable values for their sedimentation.

While the pH values range from 1.0 at min. to max 3.2, while the average is 3.2.

At first, samples were taken every 2 hours, while later every 4 hours, which is easily proven that the cleaning efficiency has been reached at a pH of 9-10.5 in the following percentages: Pb=65-80%; Zn=92-99%; Cu= 70-85%; and Cd=95-99%.

The average load values of the dirty waters are: Zn=1357mg/l; Pb=12.2mg/l; Cu=1.01mg/l and Cd=0.54mg/l. Table 2,3,4 shows results for sample no 1,2,3 respectively.

The average load values of the dirty waters are: Zn=1357mg/l; Pb=12.2mg/l; Cu=1.01mg/l and Cd=0.54mg/l. And such water quality has a high cleaning efficiency, respectively of the removal of heavy metals, which is done near pH values of 9-10.5. This means that the quality of polluted water after cleaning is as follows:

Pb= 3.58 x 0.20 = 0.72 mg/l
Zn = 1357 x 0.01 = 13.57 mg/l
Cu = 1.01 x 0.20 = 0.20 mg/l
Cd = 6.54 x 0.01 = 0.06mg/l

Now that we have the amount of wastewater, which is: Q= 33.75 m3/h = 9.2l/sec, therefore based on the results obtained above, it follows that the concentration of metals in the effluent is as follows:

Cef^{Zn} = 9.2 l/sec x 13.57 mg/l = 124.8 mg/sec
Cef^{Pb} = 9.2 l/sec x 0.72 mg/l = 6.62 mg/sec
Cef^{Cu} = 9.2 l/sec x 0.20 mg/l = 1.84 mg/sec
Cef^{Cd} = 9.2 l/sec x 0.06 mg/l = 0.55 mg/sec

4. Conclusions

With the process neutralization with slaked lime to achieve that the majority of metal ions preceptiation in the form of hydroxide.

The efficiency of heavy metals preceptiation depending on by pH value with milk lime, as follows:

Pb= 65-83%; Zn = 93-99%; Cu = 65-83% and Cd = 95-99%, so it is within the allowed limits and after preparing enabled the issuance of industrial wastewater according to the legal rules for the protection of water.

In cases when have to deal with increased alkaline during the process of neutralization, then we have to add acid melting or an amount of water industrial waste, so that the pH value to correspondence with the conditions of the working environment, as defined according to the rules of law.

In cases when have the average values of heavy metals in industrial waste water, then needed value is pH = 10.5, while in cases when have with overload process, then needed value is pH= 12.5

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- **Ethical approval:** The conducted research is not related to either human or animal use.
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