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## **PROCESSING OF INDUSTRIAL PHARMACEUTICAL SEDIMENT**

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Separate sewerage collects waters that are being discharged from all technological lines in one of pharmaceutical factories in Bulgaria. The object of this study is slightly acidic waste water having pH=4-5 which is cleaned by neutralization. The water is neutralized in a radial settler equipped with peripheral device for collecting the waste water, where it is mixed and neutralized with  $\text{Ca}(\text{OH})_2$ . Necessary amount of  $\text{Ca}(\text{OH})_2$  is added through a feeder and pump. The applied dosage is 10% higher than calculated. The mixture of  $\text{Ca}(\text{OH})_2$  and waste water settles in a horizontal thickener, where the sludge is removed and final settling of the overflow is conducted. After the final settling, cleaned water (overflow) is being treated together with the household waste in a town waste water treatment plant. The remained sludge has pH=8-9 and 50 to 60% moisture. The extracted sludge from the settling/radial primary and secondary settler/through pumps enters a special sludge pond where the sludge is stored. It contains organic and inorganic compounds as well as various chemical elements. The treatment of the sludge is object of the present article.

*Key words: wastes, neutralization, sewerage, sludge*

### **INTRODUCTION**

Two types of production waste waters are discharged by all pharmaceutical factories – polluted and the so-called conditionally clean waters. A common practice is to separate the industrial waste from the sewerage system of factories because the polluted industrial waste waters are used for circulation after cleaning.

The subject of this study is slightly acidic waste water (pH=4-5) cleaned by neutralization. This water is neutralized in a radial settler equipped with peripheral device for collecting the waste water, where it is mixed with neutralizing agent –  $\text{Ca}(\text{OH})_2$ . The necessary amount of  $\text{Ca}(\text{OH})_2$  is added through a feeder and a pump. The chosen dosage is 10% higher than the calculated one. The mixture of  $\text{Ca}(\text{OH})_2$  and waste water is subjected to settling in a horizontal thickener, where the sludge is

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removed and final settling of the overflow is conducted. After the final settling, the already cleaned water (overflow) is treated together with the household waste in a town waste water treatment plant. The remained sludge has pH=8-9 and moisture of 50 to 60%. It is extracted from the radial (primary and secondary) settler through pumps, and then, directed to a special sludge pond where the sludge is stored. It contains series of organic and non-organic compounds as well as various chemical elements. Such elements as Ni and Zn have the highest concentration in the sludge and therefore their extraction is considered to be important. Not only sludge treatment is achieved by this process but also further concentration of extracted heavy metals is possible.

Elements content in the sludge and research methodology. The content of elements in the sludge is given in Table 1.

Table 1. Content of selected elements in the sludge

Element	Pb, %	Zn, %	Cu, %	Ni, %	S, %
Concentration	0.04	5.08	0.05	1.27	5.98

Several methods for extraction of Cu, Ni and Zn from the sludge have been investigated:

1. H<sub>2</sub>SO<sub>4</sub> (5,10 and 15% solution) leaching (Table 2).
2. NaCN solid waste treatment (Table 3).
3. Stage leaching with 15% solution of H<sub>2</sub>SO<sub>4</sub> (Table 4).
4. Stage leaching with heat treatment of the rests. (Table 5).

## RESULTS AND DISCUSSION

Tables 2-5 show the results of experiments

Table 2. Sludge after leaching with H<sub>2</sub>SO<sub>4</sub> solution

№	conditions	product	volume	Grade, mg/dm <sup>3</sup> , or %			Recovery,%		
				Cu	Ni	Zn	Cu	Ni	Zn
1.	1 dm <sup>3</sup> 5% H <sub>2</sub> SO <sub>4</sub> solution	filtrate	1.030 dm <sup>3</sup>	3.7	105.8	1116	38.13	44.86	96.37
		hard rest	5.15g	0.12%	2.60%	0.84%	61.87	55.14	3.63
		input	26.80 g	0.037%	0.90%	4.44%	100.00	100.00	100.00
2.	1 dm <sup>3</sup> 10% H <sub>2</sub> SO <sub>4</sub> solution	filtrate	1.100 dm <sup>3</sup>	1.9	1.9	1096	25.83	61.87	98.57
		hard rest	6.00g	0.10%	0.10%	0.29%	74.17	38.13	1.43
		input	26.80 g	0.029%	0.029%	4.48%	100.00	100.00	100.00
3.	1 dm <sup>3</sup> 15% H <sub>2</sub> SO <sub>4</sub> solution	filtrate	1.075 dm <sup>3</sup>	3.1	123.1	1312	42.31	52.93	98.83
		hard rest	5.05g	0.09%	2.33%	0.33%	57.69	47.07	1.17
		input	26.80 g	0.026%	0.93%	5.32%	100.00	100.00	100.00

Table3. The results of NaCN solution leaching of the sludge after H<sub>2</sub>SO<sub>4</sub> solution leaching

	Conditions	Product	Volume, dm <sup>3</sup>	Containing, mg/d <sup>3</sup>			Recovery%		
				Cu	Ni	Zn	Cu	Ni	Zn
1	0.400 dm <sup>3</sup>	filtrate	0.425dm <sup>3</sup>	<4	215,9	14,4	<5.46	30.83	8.32
2	5% NaCN and 0.5% CaO.	hard rest	12.25g	0.24%	1.68%	0.55%	95.54	69.17	91.68
3		input	16.50g	0.18%	1.80%	0.44%	100.00	100.00	100.00

Table4. Results after poly-stage leaching with 15% with H<sub>2</sub>SO<sub>4</sub> solution

№	Conditions	Product	Volume, dm <sup>3</sup>	Containing, mg/d <sup>3</sup>			Recovery %		
				Cu	Ni	Zn	Cu	Ni	Zn
1	1 dm <sup>3</sup> 15% H <sub>2</sub> SO <sub>4</sub> solution one stage	filtrate	0.930dm <sup>3</sup>	5	332.2	1467	50.27	86.75	98.50
		hard rest	11.50g	0.04%	0.41%	0.18%	49.73	13.25	1.50
		input	26.90g	0.034%	1.32%	5.16%	100.00	100.00	100.00
2	1 dm <sup>3</sup> 15% H <sub>2</sub> SO <sub>4</sub> solution two stages.	filtrate	0.580dm <sup>3</sup>	4	930	3637	11.45	72.90	93.90
		hard rest1	6.55g	-	-	-	-	-	-
		hard rest2	9.75g	-	-	-	-	-	-
		common hard rest	16.30g	0.11%	1.23%	0.84%	88.55	27.10	6.10
		input	53.60g	0.037	1.38%	4.19%	100.00	100.00	100.00
3	1 dm <sup>3</sup> 15% H <sub>2</sub> SO <sub>4</sub> solution three stages	filtrate	0.420dm <sup>3</sup>	21.36	1653	7666	29.48	76.39	92.02
		hard rest1	8,32g	-	-	-	-	-	-
		hard rest2	11,25g	-	-	-	-	-	-
		hard rest 3	11,25g	-	-	-	-	-	-
		common hard rest	30.65g	0.07%	0.70%	0.91%	70.52	23.61	7.98
		input	80.40g	1.13%	1.13%	4.35%	100.00	100.00	100.00

It is evident from Table 2 that the most appropriate concentration of H<sub>2</sub>SO<sub>4</sub> solution is 10 and 15%. Nickel extraction from a solution with concentration of 10% gives better results than that of 15%, whereas copper extraction gives better results from a solution with concentration of 15% than that of 10%. Zinc extraction is constant. The differences in extraction results come from the increased concentration of the components. Due to the fact that decreased nickel extraction from a solution with concentration of 15% could not be attributed to passivation of solubility of nickel containing sludge components, we decided next experiments (sludge leaching) to be

conducted with 10% H<sub>2</sub>SO<sub>4</sub> solution. The insoluble residues from the experiments were combined and the obtained material leached with 0.15% NaCN solution (Table 3) and 0.5% CaO solution. The pH of the solution during leaching was controlled, so that it was never below 9.5. The adjustment was performed with 10% Na<sub>2</sub>CO<sub>3</sub> solution. The results in Table 3 show that after cyanation 30% of the nickel in the insoluble residue could be extracted.

The concentration of Ni and Zn in filtrate (Table 2) varies from 100 to 120 mg/dm<sup>3</sup> for Ni and 1100-1300 mg/dm<sup>3</sup> for Zn. A direct extraction by electrolysis is not possible due to the low concentrations of the metals. This is why the experiment was conducted with H<sub>2</sub>SO<sub>4</sub> solution of 15% and one or two portions of fresh waste were added to the obtained filtrate. The results in Table 4 show that by applying three stages of leaching with nickel extraction ranging from 76%-80% and zinc from 90%-92%, the Ni and Zn levels in the solution increased to 1650 mg/dm<sup>3</sup> and 7666 mg/dm<sup>3</sup>, respectively. The obtained solution from initial solutions of 76% nickel and 92% zinc could successfully be dissolved by usage of specific nickel and zinc agents (solvent extraction), thus increasing its concentration to the levels necessary for electro-winning. Thus, the solutions obtained by the three stage leaching process could be used as raw materials for nickel and zinc extraction. Organic residue was burnt at 800 °C in a hot air furnace. As a result, the extraction amount of final waste product was decreased by 65% (Table 5). The obtained product contains 2.17% Ni and 1.76% Zn and it can be used as raw material for nickel and zinc production as well. For instance, once cooled, the burnt product at 800°C was leached by 15% H<sub>2</sub>SO<sub>4</sub> solution in the presence air enriched in O<sub>2</sub>. The obtained sulfuric acid solution contained 12 g/dm<sup>3</sup> zinc and 8 g/dm<sup>3</sup> nickel.

Table 5. Results after temperature treatment of the rests

	Conditions	products	Yield γ,%	Content, %		Recovery, %	
				Ni	Zn	Ni	Zn
1.	Burning 800°C	Hard rest eliminated	34.98	2.17	1.79	97.33	97.85
2.		Eliminated proportion part	65.02	0.032	0.021	2.67	2.15
3.		input	100.00	0.78	0.64	100.00	100.00

## CONCLUSIONS

Basing on the obtained results, the following diagram (Fig. 1) can be offered, which shows the processing of waste containing Ni and Zn. It shows three stages of leaching with 15% sulfur acid. The solution is removed after each stage and a new portion is added. The overflow (a product of three-stage leaching) is filtered and the obtained filtrate is then subjected to evaporation, cooling and crystallization of NiSO<sub>4</sub> and ZnSO<sub>4</sub>.

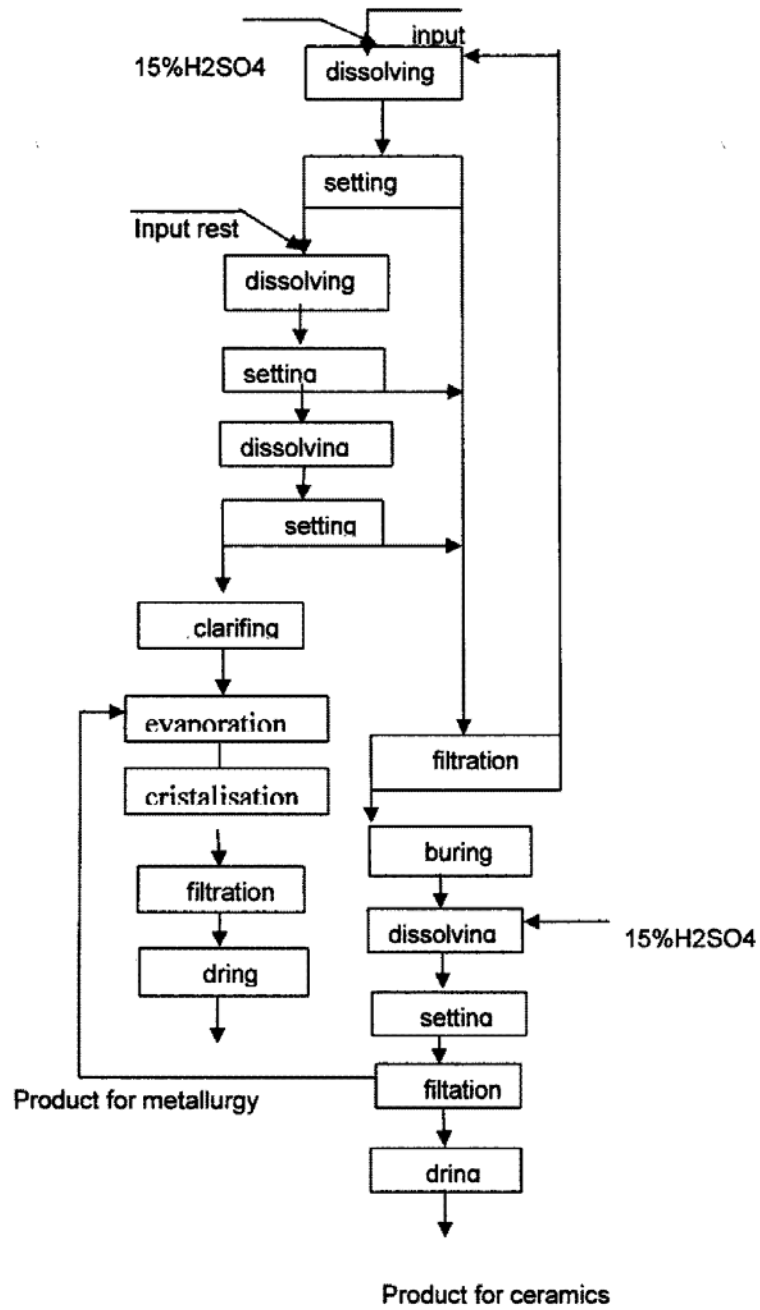


Fig.1. Flow sheet for treatment

The obtained sludge from the three-stage leaching and crystallization is then mixed and filtrated. Afterwards, the filter is returned to the first stage of leaching. After filtration, the hard residual material is burnt. The burnt residue is dissolved in 15%  $H_2SO_4$  and the obtained solution, after settling and filtration, enters the evaporation stage. The hard residual material enters the drying stage. The product obtained from drying contains traces of Ni and Zn and can be used for modifying erosive soils.

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Oddzielna kanalizacja zbiera wody odprowadzane przez wszystkie linie technologiczne jednego z zakładów farmaceutycznych w Bułgarii. Przedmiotem obecnych badań są lekko kwaśne odpadowe muły, posiadające  $pH=4-5$ , które są otrzymane przez neutralizację. Wody są neutralizowane w odstożnikach promienistych wyposażonych w peryferyjne urządzenie do zbierania wody odpadowej, gdzie jest ona mieszana i neutralizowana za pomocą  $Ca(OH)_2$ . Niezbędna ilość wapna dodawana jest przez podajnik i pompy. Zużycie odczynnika wynosi około 10% więcej niż ilość obliczona. Mieszanina  $Ca(OH)_2$  i wody odpadowej jest poddawana osadzeniu w horyzontalnych zagęszczaczach, gdzie usuwany jest szlam oraz przeprowadzany jest ostateczny oczyszczanie przelewu. Po końcowym osadzeniu, klarowna woda (przelew) jest mieszana z ściekami domowymi w miejskim zakładzie oczyszczania wody. Otrzymany muł posiada  $pH=8-9$  oraz wilgotność od 50 do 60%. Wydzielony muł pobierany jest ze wstępnych radiacyjnych i wtórnych odstożników za pomocą pomp i przesyłane jest do specjalnego stawu, gdzie jest przechowywany. Zawiera on związki organiczne i nieorganiczne, jak również różne pierwiastki chemiczne. W pracy opisano przerób tych mułów.