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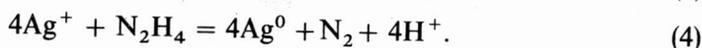
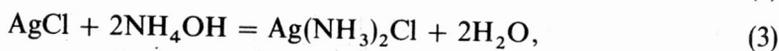
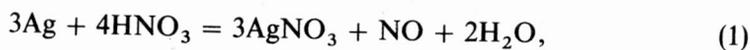
TREATMENT OF WASTEWATER FROM HYDROMETALLURGICAL REFINING OF SILVER SCRAP

Silversmithery produces scrap which comprises 93% of Ag, the remainder being Cu, Zn, Fe and Pb impurities. One of the available methods to process this type of scrap is hydrometallurgical refining. The hydrometallurgical method yields a silver power containing 99,96% of Ag, but it has the disadvantage of producing at the same time two kinds of troublesome wastes: acidic wastewater from solubilization of the silver scrap and alkaline wastewater from solubilization of silver chloride and chemical reduction of hydrazine.

The present paper gives the physicochemical composition of the wastewaters, as well as the results of technological investigations conducted in a multi-purpose treatment system (Polish patent No. 119207).

1. INTRODUCTION

Silversmithery scrap contains about 93% of Ag, the remainder being Cu, Zn, Fe, and Pb impurities. Of these, Cu accounts for about 6%. The scrap is processed either in smelters or by different hydrometallurgical methods. One of these consists of digestion with nitric acid (1), eduction of silver chloride (2), and dissolution in ammonia liquor, which yields the $\text{Ag}(\text{NH}_3)_2 \cdot \text{Cl}$ complex (3). In the presence of hydrazine, the complex decomposes to precipitate Ag(4):



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After filtering and drying, the silver powder obtained via this route contains 99.96% of Ag and trace amounts of Cu, Zn, Pb, and Fe [1].

Hydrometallurgical refining of silver scrap produces acidic and alkaline wastewaters. Acidic wastewater is generated as a result of the following processes: solubilization of silver scrap, chemical precipitation of silver chloride sediments, filtration, and washing of silver chloride. Solubilization of silver chloride, chemical reduction of Ag^+ ions, filtration and washing of metallic Ag sediments produce alkaline wastewater (tab. 1). In acidic wastewater nitric acid, sodium nitrate and

Table 1

Physicochemical composition of wastewater from hydrometallurgical refining of silver scrap

Parameter	Unit	Acidic effluent	Alkaline effluent	Mixed effluent
Turbidity	g/m^3	10	20	10
Colour	g Pt/m^3	green	40	bright blue 1:2000
Odour	—	—	specific NH_3	specific NH_3
pH	—	1.15	11.31	9.12
Total alkalinity	$\text{g CaCO}_3/\text{m}^3$	0	14000	6500
Mineral acidity	$\text{g CaCO}_3/\text{m}^3$	3735	0	0
Copper	g Cu/m^3	1140	0.4	700
Silver	g Ag/m^3	10	3.4	7.0
Zinc	g Zn/m^3	54	0.9	2.7
Lead	g Pb/m^3	4	0	1.9
Iron	g Fe/m^3	3	0	0
Sodium	g Na/m^3	4450	92	2480
Chlorides	g Cl/m^3	90	8000	3830
Sulfates	$\text{g SO}_4/\text{m}^3$	130	108	234
Permanganate COD	$\text{g O}_2/\text{m}^3$	27	210	130
Ammonia nitrogen	g N/m^3	6.2	3920	1800
Nitrite nitrogen	g N/m^3	54	0.6	60
Nitrate nitrogen	g N/m^3	3600	0	1950

cupric nitrate are dominant. In alkaline wastewater ammonium hydroxide and ammonium chloride prevail over the remaining components. The overall wastewater stream leaving the plant is a combination of acidic and alkaline wastes, and carries large amounts of chlorides, sodium nitrates, ammonium nitrates, and copper salts (in ammoniated form). Their presence is indicated by the blue colour of the effluent. Waste streams of that kind can neither be sent to the municipal sewer system nor enter a natural waterway. After removal of heavy metal ions, the effluent may be used for the biological treatment of industrial wastewater with poor nitric substance content or can be utilized as a fertilizer (a source of nitrogen compounds).

2. TREATMENT CONCEPT

The data in tab. 1 show that the acidic effluent contains far more heavy metals than the alkaline wastewater stream. Thus, the treatment concept involves 1) copper removal from the acidic stream by using file dust (and free acid contained in the wastewater) and 2) mixing of the acidic stream with the alkaline one to cause neutralization and chemical precipitation of heavy metal ions (including Fe^{3+}) in the form of slightly soluble hydroxides. Following separation of the sediments, the metal ions persisting in the wastewater may be chemically fixed and sorbed by a calcium carbonate suspension (fig. 1).

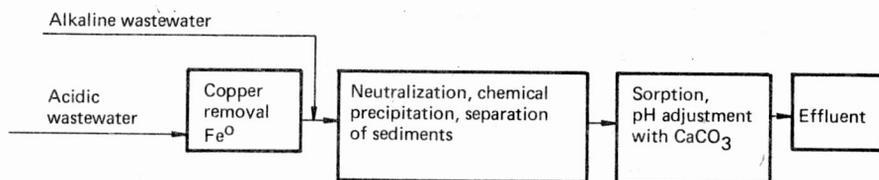


Fig. 1. Removal of heavy metal ions from wastewater produced during hydrometallurgical refining of silver scrap

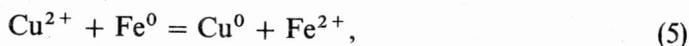
The advantages may be itemized as follows: 1) neutralization by combining acidic and alkaline wastewater streams, 2) chemical precipitation of heavy metals in the form of slightly soluble hydroxides, 3) reuse of industrial waste products, i.e., file dusts and calcium carbonate (from water softening or lime decarbonation), which act as reacting substances, and 4) no increase in the salinity level [2].

3. EXPERIMENTAL

3.1. APPARATUS

The treatment process is of a complex, heterogeneous nature. Laboratory investigations were carried out in an apparatus (fig. 2) adapted to continuous feed [3].

A peristaltic pump sends the acidic waste to column A. In the presence of file dust, copper removal and partial neutralization of free acid are achieved:



Also an increase in the content of iron ions occurs there. Like other heavy metal ions contained in the solution, iron ions are separated in the form of sediments in the course of the wastewater neutralization process (by circulation and in reactor B). The

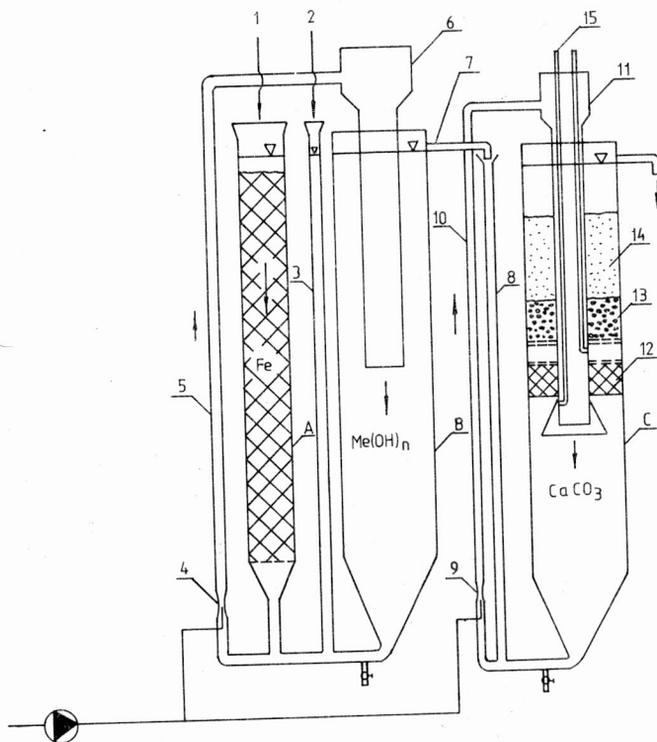
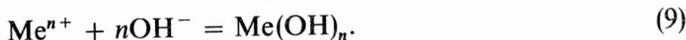
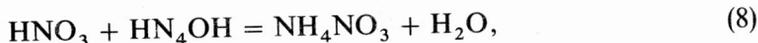


Fig. 2. Treatment system for the effluent from hydrometallurgical refining of silver scrap
 A, B, C, — reactors, 1 — inflow of acidic wastewater, 2 — inflow of alkaline wastewater, 3, 5, 8, 10 — feed pipes, 4, 9 — ejectors, 6, 11 — pipes, 12, 13 — elastic polyurethane foams, 14 — sand bed, 15 — gas separation deaerating pipe

reaction runs according to equations



Precipitated $\text{Fe}(\text{OH})_2$ is easily oxidized to $\text{Fe}(\text{OH})_3$ in the presence of dissolved oxygen:

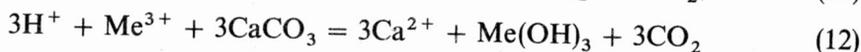
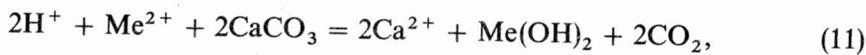


Hence, compressed air supplied to the ejector acts not only as a fluid transporting agent, but as an oxidizer as well.

A portion of the metal hydroxides sedimenting in reactor B circulates along with the wastewater; the remainder forms a kind of suspension through which the wastewater passes to the clarifying zone, situated between the reactor walls and the central pipe. At an appropriate proportion of acidic and alkaline wastes (i.e., at an

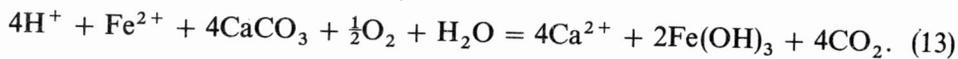
appropriate pH), a technological system consisting of column A and reactor B will suffice for the effective removal of heavy metals. The removal is not so effective if the concentration and flow rate of the circulating acidic and alkaline wastewater mixture vary with time. The rise in hydrogen ion concentrations accounts for the dissolution of metal hydroxides in reactor B, thus increasing the heavy metal content in the effluent. To eliminate this undesirable effect it is necessary to send the wastewater stream to reactor C which involves a calcium carbonate suspension, thus enabling removal of heavy metals. The alkaline suspension circulates in turbulent flow through ejector 9, delivery pipe 10, central pipe 11, and the bottom part of the cylindrical tank in reactor C. However, a certain portion of the calcium carbonate suspension remains in the sludge blanket (between the reactor wall and the central pipe). Flowing through the sludge blanket to enter the sedimentation zone and pass through polyurethane foams, the stream leaves some part of fine suspended matter in the pores and channels of the foams. Fine calcium carbonate particles present there react with the components of the wastewater stream, thus improving the treatment effect.

In reactor C, carbon dioxide (the product of free acid neutralization) is removed during turbulent flow of the suspension through the ejector, where partial pressure of gases in the fluid and in the air is equalized. Gas bubbles entering the central pipe together with circulating suspension are retained in a collector to leave the reactor through the deaerating pipe 15. Gas removal is a prerequisite to prevent floating of particles in the sludge blanket and in the sedimentation zone, and to protect the filter bed against penetration of air bubbles. Concurrently with the processes of free acid neutralization and carbon dioxide desorption, there occurs a reaction of heavy metal ions with calcium carbonate, which brings about their removal. The reaction produces slightly soluble carbonates and hydroxides:



where Me^{2+} and Me^{3+} are bivalent and trivalent metal ions, respectively.

When the wastewater stream contains Fe^{2+} ions, iron hydroxide is formed in the presence of dissolved oxygen and calcium carbonate according to the following reaction:



In fact, the chemism by which hydroxides are formed in the calcium carbonate suspension has a complex nature, and is still far from being well understood.

In the course of the treatment process (when the acidic wastewater contains heavy metal ions), the composition of the suspension undergoes changes: calcium carbonate continues to decrease, whereas slightly soluble sediments (including heavy metal hydroxides) continue to accumulate.

4. EXPERIMENTS

Laboratory tests were run in the system shown in fig. 2. The volume of column A (as well as that of cylindrical reactors) approached 2 dm^3 . After column A having been packed with file dust, reactor C filled with 80 g dry wt. of calcium carbonate, and the whole apparatus made up with tap water, continuous flow of acidic and alkaline wastewater was provided by peristaltic pumps. The flow rate of acidic wastes amounted to $193 \text{ dm}^3/\text{h}$. The flow rates of alkaline wastes were $77 \text{ dm}^3/\text{h}$, $70 \text{ dm}^3/\text{h}$, and $65 \text{ dm}^3/\text{h}$ in the first, second, and third experimental run, respectively. The rate of compressed air inflow was kept constant at the level of $46.5 \text{ dm}^3/\text{h}$ to allow circulation of the acidic and alkaline wastewater mixture at the rate of $90 \text{ dm}^3/\text{h}$ and the constant voluminal mixing ratio of the influent to the circulating mixture. The constant inflow rate of air and wastewater accounted for the constant time of wastewater retention in column A and reactors B and C (approximately 7.3 h).

Three experimental series were run for copper removal from the effluent of hydrometallurgical refining of silver scrap. The voluminal ratios of acidic to alkaline wastewater equaled 2.5:1, 2.76:1 and 2.97:1 in the first, second and third series, respectively. Physicochemical analysis was carried out for the influent and effluent of column A, reactor B, and reactor C [4], [5].

5. RESULTS AND DISCUSSION

The results are listed in tab. 2. The effluent from column A contained small amounts of Cu^{2+} , Zn^{2+} and Pb^+ and large amounts of Fe^{3+} ions (2370 to $2400 \text{ g Fe}/\text{m}^3$). Mineral acidity varied from 1235 to $1305 \text{ g CaCO}_3/\text{m}^3$ and pH was slightly higher than that of raw acidic wastes. The rise in pH and the drop in mineral acidity of the effluent from column A is an indication that a partial neutralization has been obtained. Mixing the acidic wastewater stream with the alkaline one at the 2.5:1 ratio in reactor B yields complete neutralization (the alkalinity level amounting to $45 \text{ g CaCO}_3/\text{m}^3$). The high pH of the effluent leaving reactor B should be attributed to the excess of alkaline wastes as compared to the acidic wastes. Thus, the effluent from reactor B carries only trace amounts of Cu^{2+} , Ag^+ , Zn^{2+} , and Fe^{3+} ions (tab. 2). Further treatment (series 1) with calcium carbonate suspension in reactor C is useless. But, when the acidic to alkaline wastewater ratio fails to yield complete neutralization (the mixture displays an acid pH, as in series 2 and 3, and large amount of Fe^{3+} ions, ranging between 218 and $385 \text{ g Fe}/\text{m}^3$), the stream is to be passed to reactor C, containing a calcium carbonate suspension, for complete neutralization and iron removal (tab. 2, experimental series 2 and 3). The effluent from reactor C displays a weak alkaline pH, a low total alkalinity, and very low concentrations of heavy metal ions (if at all).

Table 2

Treatment efficiencies

Exper. series	Dur-ation of days	Voluminal ratio of acidic to alkaline wastes	pH	Acid-ity g CaCO ₃ /m ³	Alka-lin-ity	Metal ion content				
						Copper	Silver	Zinc	Lead	Iron
Acidic influent										
1-3	—	—	1.16	3735	0	1140	10	54	4	3
Alkaline influent										
1-3	—	—	11.31	0	14000	0.4	3.4	0.9	0	0
Effluent from column A										
1	2	acidic	1.62	1235	0	0.58	0	2.29	0.20	2400
2	2	waste-water alone	1.62	1275	0	0.65	0	1.38	0.20	2380
3	2		1.61	1305	0	0.87	0	1.31	0.15	2370
Effluent from reactor B										
1	2	2.50:1	10.63	0	45	0.27	0.21	0.35	0.08	0.1
2	2	2.76:1	4.54	335*	0	0.62	0.26	1.24	0.17	218
3	2	2.97:1	4.46	610*	0	0.74	0.37	1.36	0.27	385
Effluent from reactor C										
1	2	2.50:1	9.53	0	70	0.12	0	0.20	0	0.05
2	2	2.76:1	7.86	0	80	0.11	0	0.03	0	0.08
3	2	2.97:1	7.71	0	90	0.10	0	0.24	0	0.14

* Total acidity, with no Fe³⁺ ion concentration correction.

6. CONCLUSIONS

1. Hydrometallurgical refining of silver scrap produces acidic and alkaline wastewaters contaminated with nitrogen compounds and heavy metal ions.
2. The effluent from metallurgical refining requires copper removal before it is used for agricultural or any other purposes (e.g., biological treatment).
3. Good treatment effects are achieved as a result of the following processes: heavy metal removal, neutralization by mixing acidic and alkaline wastewaters at an appropriate voluminal ratio, sorption, and pH adjustment by using calcium carbonate suspensions.
4. The processes included in item 3 are carried out in the system of three reactors enabling continuous flow and yielding good treatment efficiencies.

5. The method proposed has two major advantages: 1) neutralization is achieved by mixing two types of wastewater with no addition of chemicals 2) two waste products, i.e., fine dust and calcium carbonate, are used for heavy metal removal.

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OCZYSZCZANIE ŚCIEKÓW Z HYDROMETALURGICZNEJ RAFINACJI ZŁOMU SREBROWEGO

Złom srebra z wyrobów jubilerskich zawiera 93% Ag, pozostałe 7% to domieszki Cu, Fe, Zn i Pb. Jedną z metod oczyszczania tego złomu jest metoda hydrometalurgiczna. W procesie oczyszczania powstaje srebro o zawartości 99,96% czystego metalu oraz ścieki kwaśne (z rozpuszczania złomu) i zasadowe (z rozpuszczania AgCl i redukcji hydrazyną). Podano skład fizyczno-chemiczny tych ścieków oraz wyniki badań technologicznych nad ich oczyszczaniem w urządzeniu wielofunkcyjnym (patent 110207).

ОЧИСТКА СТОЧНЫХ ВОД, ВОЗНИКАЮЩИХ ВО ВРЕМЯ РАФИНАЦИИ СЕРЕБРЯНОГО ЛОМА

Серебряный лом из ювелирных изделий содержит 93% Ag, остальные 7% это примеси Cu, Fe, Zn и Pb. Одним из методов очистки этого лома является гидрометаллургический метод. В процессе очистки возникает серебро содержания 99,96% чистого металла, а также кислые (из растворения лома) и основные (из растворения AgCl и редукции гидразином) сточные воды. Дан физико-химический состав этих сточных вод, а также результаты технологических исследований их очистки во многофункциональной установке (патент 110207).