

CHROMSYMP. 823

## SELECTIVE SEPARATION OF COMPONENTS [COPPER, NICKEL, ZINC, CHROMIUM(VI)] IN THE PROCESS OF ION-EXCHANGE PURIFICATION OF WASTE WATERS

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### SUMMARY

An ion-exchange method has been developed to purify the acidic waste water of non-ferrous metals treatment plants [the wash water of pickling shops containing Cu, 50-120; Zn, 70-250; Ni, 3-25; Cr(III) 30-100; Cr(VI), 20-70 mg/ml; free H<sub>2</sub>SO<sub>4</sub> 0.3-2.5 g/l; pH = 1.5-2.5] has been implemented in a number of industrial plants. The acidic waste water was purified by extracting successively a part of the components on Soviet-made selective sorbents and separating the rest of them chromatographically.

The elaborated purification method with the use of selective sorbents allows to obtain single-component concentrated solutions and all the components of sewage as commodity products during the regeneration.

The purified water is returned into the washing baths of the etch departments of the factory and is used for washing of non-ferrous metals and their alloys after the etching.

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### INTRODUCTION

The basic trend in waste water purification at present is the development of methods that provide the possibility of utilizing the components extracted from waste waters, in addition to the recirculation of purified water. One of the methods that make possible the return of purified water for production needs and the utilization of waste water components is ion-exchange purification, which has recently found extensive application in purifying waste waters of different composition<sup>1-3</sup>.

To render harmless the acidic waste water from non-ferrous metals treatment (NFMT) plants (the wash water from pickling shops), the ion-exchange purification method<sup>4,5</sup> has been developed and implemented in a number of industrial plants. Acidic waste water, together with pickling solution effluents, account for not more than 5% of the overall discharge of waste waters from the plant, but owing to the

nature of the contaminants these are the most toxic discharges from the plant. The content of metal ions and acids is many times higher than the MPC and varies within the following limits: Cu, 50–120; Zn, 70–250; Ni, 3–25; Cr(III), 30–100; Cr(VI), 20–70 mg/l; free  $H_2SO_4$ , 0.3–2.5 g/l;  $pH = 1.5–2.5$ .

The ion-exchange purification of acidic waste waters involves extracting all the solution components on KU-2-8 ( $H^+$ ) cation exchange and AV-17-8 ( $OH^-$ ) anion exchanger, recirculating the pure water into the rinse baths of the plant pickling shops, regenerating the spent sorbents and reprocessing the eluates formed, with partial utilization of the extracted waste water components.

Experience gained during the operation of the acidic waste water ion-exchange purification plants has revealed the complexity of the developed methods for reprocessing the concentrated regeneration solutions and the impossibility of the complete utilization of the components extracted from the waste water. In addition, during operation a number of difficulties arose, associated with, amongst other things, the presence of chromium(VI) in the acidic waste water. Chromium(VI), when sorbed on AV-17-8 anion exchanger, gradually destroyed it both chemically and mechanically, which finally resulted in the necessity for its complete replacement.

To achieve a more efficient ion-exchange purification of the acidic waste water from pickling shops and to ensure the implementation of a practically waste-free procedure, the previously developed scheme was substantially improved. In contrast to the initial scheme, the acidic waste water components were now separated during their purification by extracting successively part of the components on selective sorbents and separating the remainder chromatographically (Fig. 1).

The first to be separated from the other solution components is chromium(VI). For its selective extraction, the weakly basic pyridine-containing AN-251 anion exchanger<sup>6</sup> was used, known from literature for its selectivity towards chromates<sup>7,8</sup>. The separation of chromium(VI) from the other acidic waste water components is

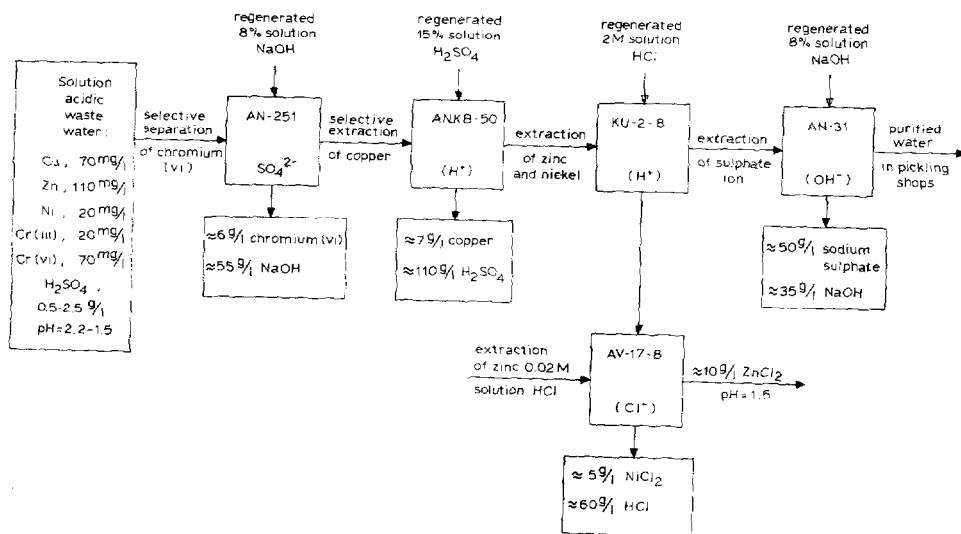


Fig. 1. Technological scheme of selective ion-exchange purification of acidic waste water in non-ferrous metal processing plants.

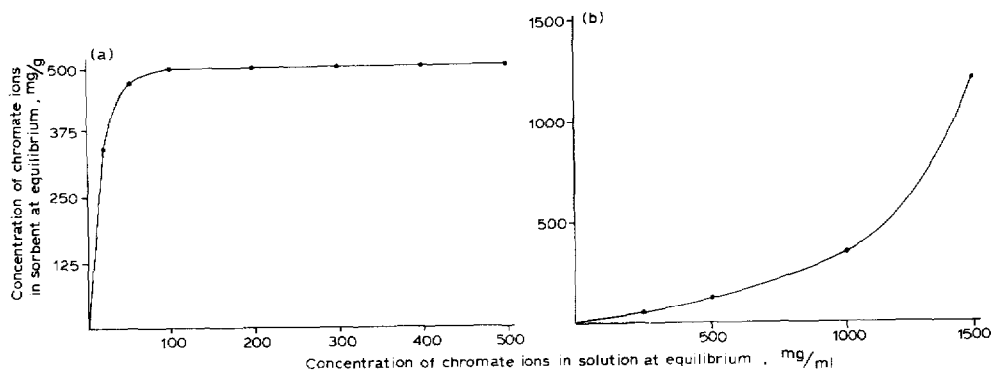


Fig. 2. Isotherms of the sorption of chromate ions on AN-251 anion exchanger in (a) the sulphate and (b) the hydroxyl form.

most effectively achieved on the AN-251 ( $\text{SO}_4^{2-}$ ) anion exchanger. The sorption isotherm of chromate ions on this exchanger is very convex, almost rectangular, whereas the sorption isotherm on AN-251 ( $\text{OH}^-$ ) anion exchanger is concave (Fig. 2). Using dynamic output curves, it was shown that chromate sorption on AN-251 ( $\text{SO}_4^{2-}$ ) anion exchanger is determined by the regularities of external diffusion. This is also confirmed by the fact that equilibrium in this process is established within 2 h (Fig. 3). The good kinetic properties of the sorbent make it possible to extract chromium(VI) at a flow-rate of 10–15 m/h. Fig. 4 shows the output curves of the selective separation of chromium(VI) from copper, zinc and nickel ions on AN-251 ( $\text{SO}_4^{2-}$ ) anion exchanger, obtained on a semi-commercial plant. It can be seen that chromium(VI) is quantitatively separated from the non-ferrous metal ions. The sorbent capacity in this instance was 80–100 mg of chromium(VI) per 1 g of dry sorbent.

AN-251 anion exchanger can be regenerated with 8% sodium hydroxide solution, with 10–15 volumes (*ca.* 15 equiv. per exchange capacity equivalent) spent per volume of swollen sorbent.

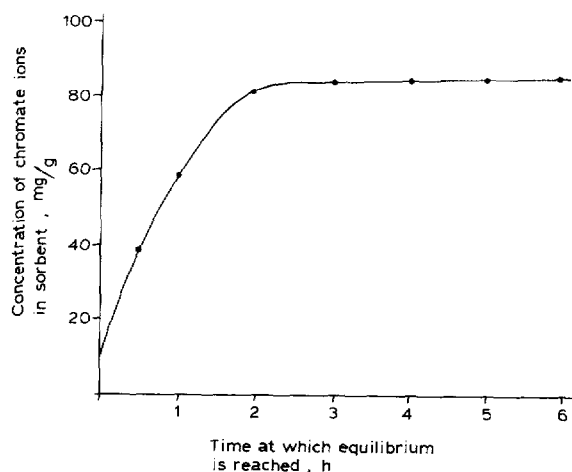


Fig. 3. Dependence of the extent to which equilibrium is reached on the contact time in the sorption of chromate ion on AN-251 ( $\text{SO}_4^{2-}$ ) anion exchanger.

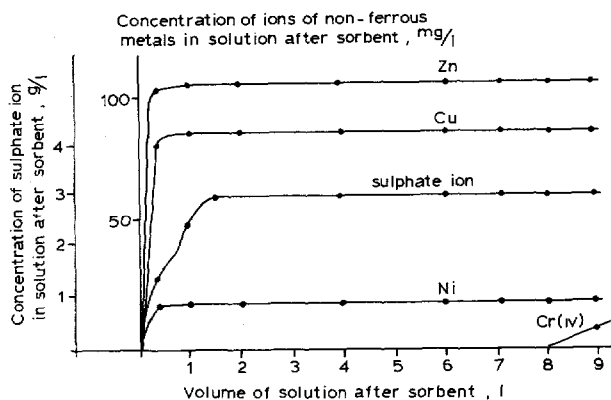


Fig. 4. Output curves of selective chromium(VI) separation from the other components of acidic waste water on AN-251 ( $\text{SO}_4^{2-}$ ) anion exchanger.

For the selective extraction of copper after chromium(VI) separation, we used ANKB-50 ( $\text{H}^+$ ) aminocarboxylic polyampholite<sup>9</sup>. Conditions were selected for almost complete separation of copper from zinc and nickel, *viz.*, a free sulphuric acid concentration of 2.0–2.5 g/l, which corresponds to a solution pH of 1.6–1.5. To study the selective sorption of copper from the acidic waste water, we determined the distribution coefficients of copper, zinc and nickel ions on ANKB-50 ( $\text{H}^+$ ) with variation of the free sulphuric acid concentration corresponding to the levels in real solutions, from 0.5 to 2.5 g/l<sup>10</sup>. The data obtained showed that the copper distribution coefficients at all the free sulphuric acid concentrations studied exceeded considerably the zinc and nickel distribution coefficients, and at a free sulphuric acid concentration of 2.5 g/l (pH = 1.5–1.55) the copper distribution coefficient is two orders of magnitude higher than those for zinc and nickel (Fig. 5).

The copper distribution coefficient decreases insignificantly with increase in solution acidity, whereas the zinc and nickel distribution coefficients decrease by

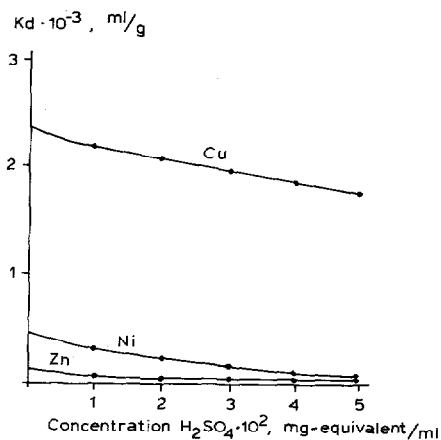


Fig. 5. Dependence of the distribution coefficients for copper, zinc and nickel on the free sulphuric acid concentration in solution in sorption on ANKB-50 ( $\text{H}^+$ ) polyampholite.

TABLE I

STABILITY CONSTANTS ( $K$ ) FOR THE COMPLEXES FORMED BY COPPER, ZINC AND NICKEL IONS WITH THE ACTIVE GROUPS OF ANKB-50 POLYAMPHOLITE

$pH$	$\log K (n = 2)$		
	$Cu^{2+}$	$Ni^{2+}$	$Zn^{2+}$
1.50	3.40	—	—
1.64	4.0	2.14	1.37
1.84	4.7	3.06	2.20

approximately one order of magnitude. All this makes it possible to conclude that the chosen sorbent is highly selective towards copper ions during sorption from the investigated solution.

From the results of potentiometric titration we calculated the stability constants of complexes formed by copper, zinc and nickel ions with the polyampholite active groups. The data obtained (Table I) show that the affinity of ANKB-50 polyampholite to copper ions is much stronger than that to nickel and zinc, as the stability constant for copper-ion exchanger complexes is an order of magnitude higher than that for the corresponding nickel complexes and two orders of magnitude higher than that for the zinc complexes.

These differences in the distribution coefficients and stability constants indicate the possibility of using ANKB-50 polyampholite for the selective sorption of copper ions from sulphuric acid solutions containing copper, zinc and nickel ions.

Fig. 6 shows the output curves for the sorption of copper, zinc and nickel ions from acidic waste water solutions on ANKB-50 ( $H^+$ ) polyampholite, obtained under factory conditions in a pilot plant. Copper is quantitatively separated from the other solution components, zinc and nickel ions, whose concentrations in the filtrate after ANKB-50 polyampholite treatment are almost equal to their initial concentrations. To improve the sorption kinetic properties of ANKB-50 polyampholite we modified

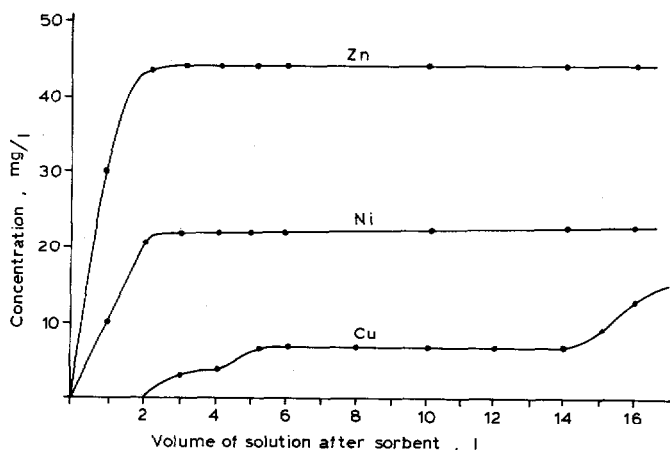


Fig. 6. Output of the sorption of copper, zinc and nickel ions from acidic waste water solution on ANKB-50 ( $H^+$ ) polyampholite.

the sorbent by mechanical processing. Copper can be separated from zinc and nickel on ANKB-50 polyampholite at a flow-rate of 5–10 m/h, which is acceptable for a technological process. The modified sorbent capacity with respect to copper is 3–5 times higher than for the unprocessed sorbent and is 1.0–1.5 mg-equiv./g dry matter.

A great advantage of ANKB-50 polyampholite, when used in the technological scheme for waste water purification, is its good regenerability. It is quantitatively (90–95%) regenerated with 15% sulphuric acid solution, with 3–5 volumes being spent per volume of swollen sorbent (5–6 equiv. per equivalent exchange capacity).

After selective extraction of chromium(VI) and copper from the acidic waste water solution, zinc and nickel remain in it. When it is necessary to separate the latter, one should use the ability of these ions to form anion exchanger–chloride complexes. All non-ferrous metal ions are known<sup>11</sup> to be capable of forming anionic chloride complexes in hydrochloric acid solutions of varying concentration. Zinc ions form stable chloride complexes in 2 *M* hydrochloric acid solutions. Nickel, however, forms unstable complexes only in 12 *M* hydrochloric acid solutions. Using the different behaviours of zinc and nickel ions in hydrochloric acid solutions, we have developed a method for their separation.

Zinc and nickel ions remaining in solution after chromium(VI) and copper have been separated on selective sorbents were jointly sorbed on KU-2-8 (H<sup>+</sup>) cation exchanger. The used cation exchanger was regenerated with 2 *M* hydrochloric acid, with 4–5 volumes being spent per volume of swollen sorbent. The solution of zinc and nickel in hydrochloric acid formed during regeneration was passed through AV-17-8 or EDE-10P (Cl<sup>-</sup>) anion exchanger. In ref. 12 it was noted that the sorption of metals with anion exchangers from solutions of complex-forming reagents is determined by two characteristics: the stability constant and the exchange constant of the anionic complexes. Also cited there is the order of the stabilities of anionic chloride complexes of non-ferrous metals: Cd > Zn > Cu > Co > Mn > Ni, from which it follows that the most stable complexes are formed by zinc and the least stable by nickel. This is in good agreement with the results of our investigations. In Table II it is shown that, on both AV-17-8 and EDE-10P anion exchangers, zinc that has passed into anionic complexes of the [ZnCl<sub>3</sub>]<sup>-</sup> and [ZnCl<sub>4</sub>]<sup>2-</sup> types in 2 *M* hydrochloric acid is almost completely separated from nickel, being sorbed on the anion exchanger. After the anion exchanger an almost single-component nickel chloride solution flows out.

Anionic chloride complexes of zinc are easily washed from the anion exchanger with water or 0.02 *M* hydrochloric acid; for the latter one can use the water used to wash the KU-2-8 cation exchanger after its regeneration with hydrochloric acid. As shown in Table II, this results in zinc being almost completely washed off, and the solution formed constitutes a single-component zinc chloride solution with the impurities of non-ferrous metal ions not exceeding 25 mg/l.

Thus, chromium(VI) and copper extraction on selective sorbents, followed by zinc and nickel from the hydrochloric acid eluate from the cation exchanger being chromatographically separated on the anion exchanger, achieves the separation of acidic waste water components during purification. This makes it possible to obtain after regeneration single-component concentrated solutions that can be reprocessed by simple technological methods for the components of acidic waste water to be utilized as commodity products in various branches of industry.

TABLE II  
SEPARATION OF ZINC AND NICKEL WITH KU-2-8 CATION EXCHANGER

The hydrochloric acid eluate is passed through AV-17-8 and EDE-10P ( $\text{Cl}^-$ ) anion exchanger. Composition of the cation exchanger regeneration hydrochloric acid solution supplied to the anion exchanger (mg/l): Ni, 900; Cu, 100; Zn, 2800; Cr(III), 100;  $\text{HCl}_{\text{free}}$ , 50–60 g/l.

	<i>Anion exchanger</i>	
	<i>AV-17-8</i>	<i>EDE-10P</i>
Composition of solution flowing out after anion exchanger in the chloride form (mg/l)	Ni 850 Cu 80 Zn 20 Cr(III) 75	Ni 820 Cu 75 Zn 30 Cr(III) 80
Composition of solution resulting from washing the anion exchanger with 0.02 M hydrochloric acid (mg/l)	Ni 5 Cu 10 Zn 2500 Cr(III) 15	Ni 10 Cu 5.5 Zn 2700 Cr(III) 25

Moreover, the separation of chromium(VI) on a selective sorbent (AN-251) prevents its coming into contact with the anion exchanger, which is designed to sorb the anionic part of the acidic waste water solution (the sulphate ion) and eliminates the technological difficulties associated with it.

For the sorption of the anionic part of the solution is recommended to use the weakly basic AN-31 anion exchanger instead of the strongly basic AV-17-8 anion exchanger used in operating purification plants. It has been found that the capacity of AN-31 for the sorption of sulphate ion is three times higher than that of AV-17-8 and the amount of alkali spent on the regeneration of AN-31 anion is four times than that needed for the regeneration of AV-17-8 (2 compared with 10–12 equiv. per equivalent of exchange capacity)<sup>13</sup>. Optimization of the process of sorbing the anionic part of acidic waste water on AN-31 and AV-17-8 anion exchangers showed the value of the "optimality criterion" for sorption of sulphate ion on AN-31 to be eight times smaller than that for the sorption on AV-17-8 (the "optimality criterion" is related to specific costs, including the capital and the operating costs).

The solution resulting from AN-31 regeneration with 8% sodium hydroxide solution constitutes a single-component alkaline solution of sodium sulphate. Its reprocessing yields technical-grade sodium sulphate, which can be used in technological processing in integrated pulp-and-paper mills.

An almost waste-free technology has thus been developed for acidic waste water treatment in non-ferrous metal plants, providing the possibility of recirculating purified water, achieving chromatographic separation of acidic waste water components during purification, reprocessing by simple technological methods the single-component solutions of selective sorbent regeneration and obtaining commodity products that can be used in various branches of industry.

The developed technological scheme can be applied to the purification of waste waters of complex composition. Its individual components (selective extraction of chromium or copper) can be used in local waste water treatment.

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