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ION EXCHANGE METHOD FOR RECOVERY OF WATER AND CHEMICALS FROM INDUSTRIAL WASTEWATER

General rules of receiving certain constituents from wastewater for industrial purposes have been presented. In particular the ion exchange methods for recycling ammonia, nitrates and water from ammonium nitrate processing, recovery of ammonia and water from ammonia processing, recovery of water and chromates or chromic acids from plating effluent as well as recovery of water and chemicals from wastewater from active metal oxides processing have been discussed.

The 50% solutions of nitric or sulphuric acids were used for regeneration of a cation exchanger bed, and 30% solution of sodium hydroxide or 20% solution of ammonia was used for regeneration of an anion exchanger bed. It allowed to obtain the adequate concentration of regeneration solutions for direct recycling to technological processes.

1. INTRODUCTION

It is well known that the pollution of natural environment is to great extent due to final and intermediate products and by-products of industrialization. These pollutants are transferred to the environment by water, huge amounts of which are used for various purposes in industry. Direct consumption of water during processing of products is as a rule relatively small, but the effluent from an industrial plant contains many chemicals which are often toxic for water environment.

Permanent increase of production results in growth of the total amount of inorganics contaminating the environment. That is why the self-purification capacity of surface water has been dangerously limited. Therefore, the main task of environment protection is, above all, to remove chemicals from wastewater.

Because of diminished reserves of fresh water more and more attention has been lately paid to its recycling. In result, much interest has been focused upon these technologies in which wastewaters are treated to such an extent that the recovered water be recycled bringing, thus, many economical effects.

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Less attention is paid to recovery of chemicals contained in wastewaters, since this procedure is conditioned by a proper separation method. The value of those substances is usually low and therefore the economic motives are not strong enough.

It should be born in mind, however, that unreproductible raw materials are getting quickly exhausted. Therefore much more attention should be paid to the recovery of chemicals from wastewater in order to decrease the consumption of raw materials, the more so as in some processes the losses of raw materials and final products are extremely high.

Processing of nitrogen compounds can be an example. For instance, about 0.3% of the produced ammonia is discharged to the environment. In 1978, production of ammonia in Poland reached 20,24,000 tons, which means that 6,072 tons of ammonia passed to the environment. Losses of nitric acid are still higher and reach 1.3%, which means that about 27,470 tons of acid penetrate into the environment. (Annual production of nitric acid in Poland was 2,113,000 tons in 1978.) The recovery of such amounts of nitrogen compounds should not be neglected.

The best solution to wastewater problems would be full recycling of water and chemicals to technology, which is illustrated by the ideograph in fig. 1.

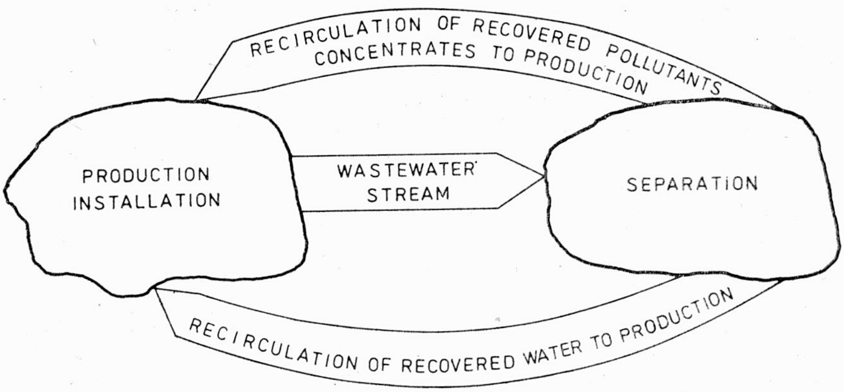

Fig. 1. Full recycling of wastewater constituents to technological process
Rys. 1. Pełna recyrkulacja składników ściekowych do procesu technologicznego

Suitable separation techniques to obtain the pollutants in concentrations allowing their recycling is the most important problem to be solved. One of the methods is ion exchange which has so far been used only sporadically for recovery of water and chemicals from wastewater.

2. GENERAL DESCRIPTION OF ION EXCHANGE

Standard ion exchangers occur in two forms (gel or macroporous type.) Since they are synthetized by different methods, their chemical and structural properties are different. Some methods of synthesis, especially crosslinking of matrix, affect swelling and shrinking of ion exchanger beds as well as their resistivity to osmotic shock. Therefore the selection of ion exchange resins appropriate for individual processes is one of the most important tasks that conditions successful application of ion exchanger in recovery of water and chemicals from wastewater.

The presented basic mechanism of ion exchange process of sorption and regeneration with highly concentrated solutions does not differ from the known mechanisms.

The way of removal of the specific ionic pollutants from water environment depends above all on the composition and kind of other pollutants and degree of their removal. In general, three groups of wastewaters can be distinguished:

1. wastewater containing a complex composition of ions, of which only one kind has to be removed,
2. wastewater containing a simple composition of ions, all of which have to be removed,
3. wastewater containing a complex composition of ions, all of which have to be removed.

From the above it follows that application of ion exchange refers to two processes, namely: selective sorption and full demineralization. These processes will be described in the following part of the paper.

2.1. SELECTIVE REMOVAL OF IONIC POLLUTANTS

It is often necessary to remove from the mixture contained in wastewater only one kind of ionic pollutants because of its toxicity or value. Generally speaking, the application of ion exchange method to this purpose allows to replace the undesired ions by other neutral ones for the environment. The principle of these methods is illustrated in the ideograph (fig. 2).

2.2. FULL DEIONIZATION

In many industrial plants one can separate wastewater containing only ions that should be removed. These are chiefly various condensates. In this case a full deionization is the best way of treatment allowing to produce demineralized water directly from the given wastewater. A general description of such a process is presented in the ideograph (fig. 3).

A direct recycling of the regeneration effluent to production is possible only when its concentration is high enough, this may be achieved, among others, by evaporation. However, evaporation is an inconvenient and expensive process being connected with the construction of special equipment and high energy consumption.

In view of the above, the methods allowing to obtain the concentration of the regeneration effluent directly from an ion exchange unit is of great importance. One of them is regeneration of ion exchange beds by applying a concentrated solution.

3. A REVIEW OF ION EXCHANGE METHODS FOR RECOVERY OF CHEMICALS AND WATER FROM WASTEWATER

The described procedures for the application of ion exchange to the recovery of water and chemicals from wastewater have been used to solve the wastewater problems in nitrogen industry, plating plants and in production of active metal oxides on an industrial scale. The concentrated mineral acids and bases used for regeneration of ion exchange resins allowed to obtain highly concentrated regeneration effluents, suitable for direct recycling into production.

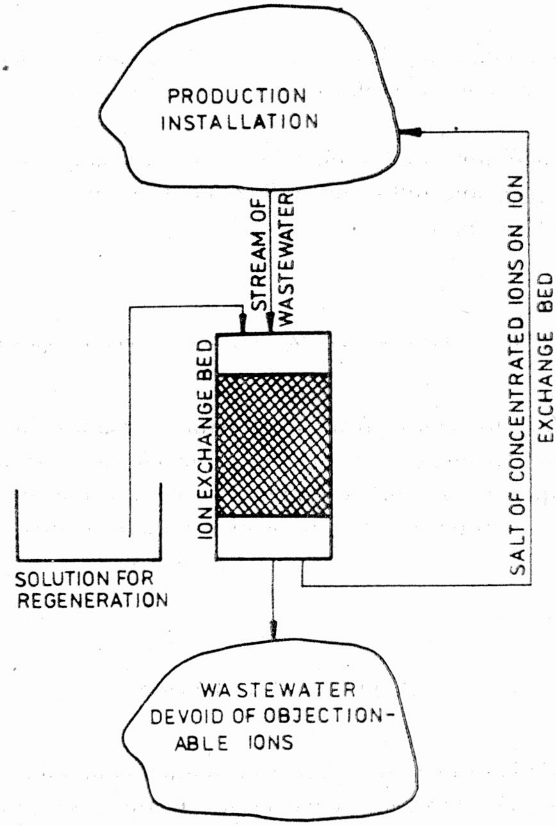

Fig. 2. Recycling of selected wastewater constituents to technological process by ion exchange method

Rys. 2. Jonitowa metoda zawracania wybranych składników do procesu technologicznego

3.1. RECYCLING OF AMMONIA, NITRATES AND WATER FROM WASTEWATER COMING FROM NITROGEN INDUSTRY

There are two kinds of wastewater of nitrogen plants which may be treated by ion exchange, i.e. wastewater from ammonia and ammonium nitrate processing. The latter (condensate) contains 500-3,000 mg of ammonium ions/dm^3 and 400-3,500 mg of nitrate ions/dm^3, whereas the former (condensate) contains 100-6,000 mg of ammonium carbonate/dm^3 as the main pollutant and small amounts of sulphate, chloride, cuprous, cupric and vanadic ions.

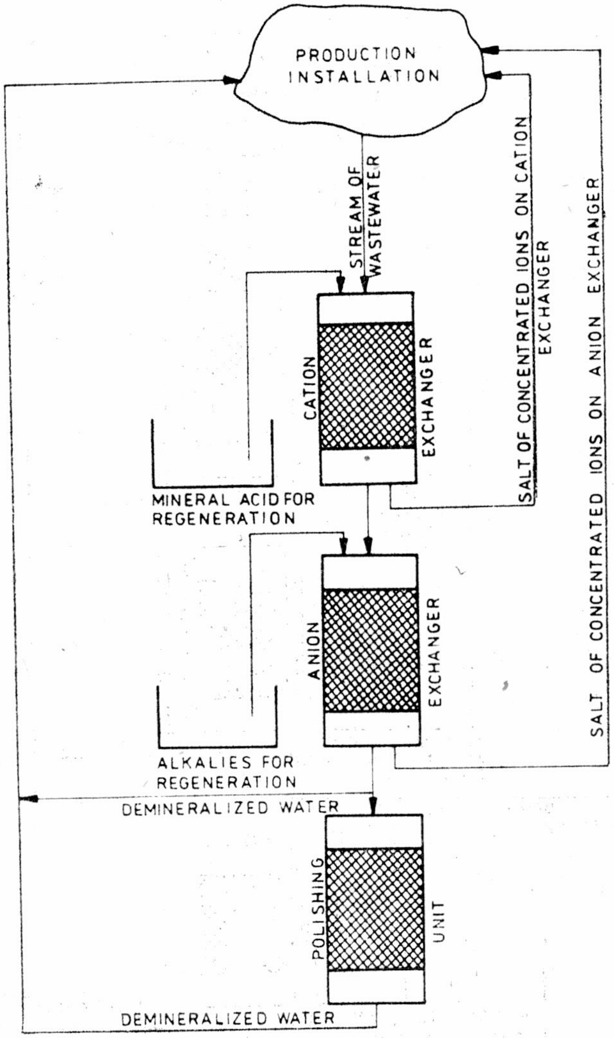

Fig. 3. Recycling of all wastewater constituents to technological process by ion exchange method
Rys. 3. Jonitowa metoda recyrkulacji wszystkich składników ściekowych do procesu technologicznego

Different ion exchange systems were designed for purification of these wastewaters, one for wastewater from processing of ammonium nitrate is presented in fig. 4. After removing suspended matter on a gravel–sand filter a raw wastewater is at first decationized on a strongly acid cation exchange bed (Amberlite 200), then it is directed onto a weakly basic ion exchange bed (Amberlite IRA-94S), where nitrate ions are sorbed. Finally, rough demineralized water is produced (its specific resistivity is about 50,000 ohms-cm).

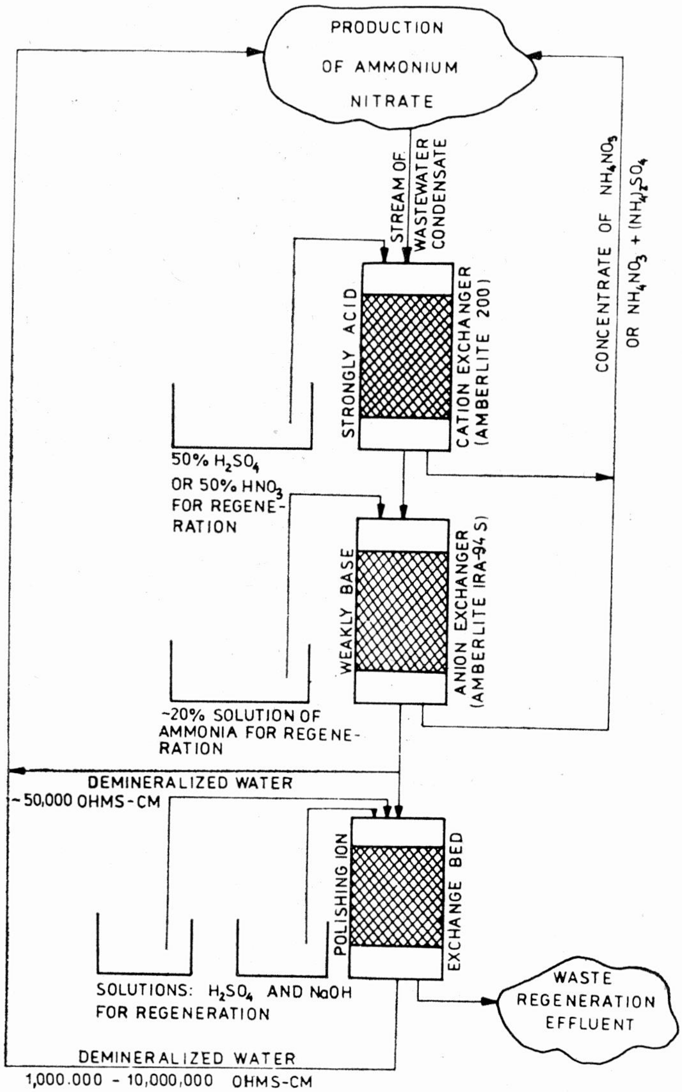

Fig. 4. Recycling of ammonia, nitrates and water from wastewater of ammonium nitrate processing to technological process by ion exchange method

Rys. 4. Jonitowa metoda zawracania amoniaku, azotanów i wody ze ścieków z produkcji saletry amonowej do procesu technologicznego

In case when a more demineralized water is required, a polishing ion exchange unit is used. To this end a mixed bed or a two-column system may be used, the first volume being filled with a strongly acid cation exchanger, while the other — with a strongly basic anion exchanger (type I). The specific resistance of the obtained water, depending on the system used, ranges from 1,000,000 to 10,000,000 ohms-cm.

For the regeneration of the first cation exchange bed, 50% nitric or sulphuric acid is used, whereas in the regeneration of the weakly base anion exchange bed 20% solution of ammonia is employed. The regeneration effluents are recycled to production.

Typical technological parameters are given in tab. 1. The ion exchange polishing bed

Table 1

Technological parameters typical of the ion exchange method for recycling water, ammonia and nitrates from wastewater of ammonium nitrate processing

Typowe parametry technologiczne metody wymiany jonowej w recyrkulacji wody, amoniaku i azotanów, które pochodzą ze ścieków powstałych podczas przetwarzania azotanu amonu

1. Regeneration of cation exchange bed (Amberlite 200) with 50% HNO_3

Regeneration agent	Dose of regeneration agent (eq/dm³ of ion exchange resin)	Compound formed	Concentration of regeneration effluent (percentage by volume and weight)		Volume of regeneration effluent (bed volumes)	Ion exchange capacity (eq/dm³ of ion exchange resin)	Volume of decationized wastewater (bed volumes)
			before neutralization with gaseous ammonia	after neutralization with gaseous ammonia			
1	2	3	4	5	6	7	8
HNO_3	1.46	NH_4NO_3	18.7	25.4	0.450	1.050	$1.050/C_{NH_4}^{*}$

2. Regenaration of cation exchange bed (Amberlite 200) with 50% H_2SO_4

5	2	3	4	5	6	7	8
H_2SO_4	1.46	$(NH_4)_2SO_4$	13.5	19.2	0.445	0.895	$0.895/C_{NH_4}^{*}$

3. Regeneration of anion exchange bed (Amberlite IRA-94S) with 20% NH_3

1	2	3	4	5	6	7	8
NH_3	1.10	NH_4NO_3	19.3	26.3	0.330	1.020	$1.020/C_{NO_3}^{**}$

* C_{NH_4} — concentration of ammonium ions in raw wastewater (as eq/dm³).

** C_{NO_3} — concentration of nitrate ions in decationized wastewater (as eq/dm³).

is regenerated in the same way as in conventional systems of water demineralization. A small amount of secondary wastewater, being an effluent from regeneration of polishing bed, is discharged to the sewer.

The process of treatment of wastewater from ammonia processing is presented in fig. 5. Here, wastewater after filtration is, as previously, decationized by a strongly acid

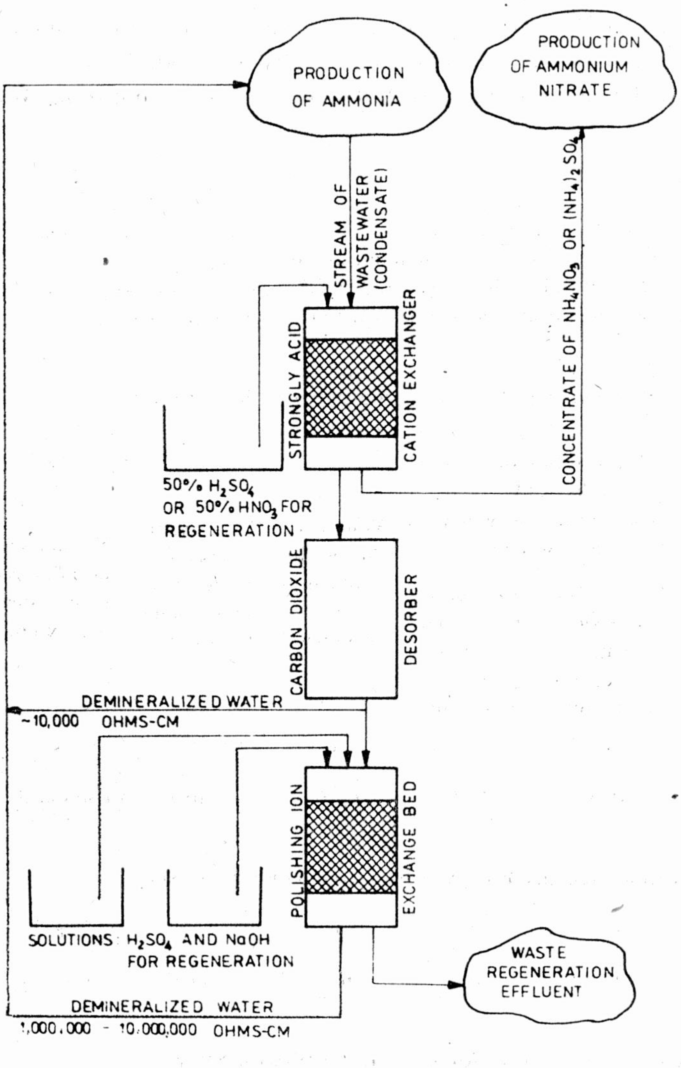

Fig. 5. Recycling of ammonia and water from wastewater of ammonia processing to technological process by ion exchange method
Rys. 5. Jonitowa metoda zawracania amoniaku i wody ze ścieków z produkcji amoniaku do procesu technologicznego

cation exchange bed (Amberlite 200). Because of high concentration of carbonates the use of carbon dioxide desorber is beneficial. Specific resistance of water after decarbonization is about 10,000 ohms-cm. It can be recycled directly to production processes or it can be directed onto an ion exchange polishing bed if more deeply deionized water is required. As a polishing unit a mixed bed unit or two-column system may be used, the first being filled with a strongly acid cation exchanger, and the other with a strongly basic anion exchanger (type I). After polishing, water reaches its specific resistance of the order of 1,000,000 to 10,000,000 ohms-cm.

The first cation exchange bed is regenerated with 50% nitric or sulphuric acid. The regeneration effluent obtained is recycled to processing of ammonium nitrate. As a rule ammonium nitrate is manufactured in the same plant as ammonia. The typical technological parameters are given in tab. 2. Regeneration of the ion exchanger polishing bed is the same as in demineralization of water.

Table 2

Technological parameters typical of ion exchange method for recycling water and ammonia from wastewater of ammonia processing

Typowe parametry technologiczne metody wymiany jonowej w recyrkulacji wody i amoniaku, które pochodzą ze ścieków powstałych podczas przetwarzania amoniaku

1. Regeneration of cation exchange bed (Amberlite 200) with 50% HNO_3

Regeneration agent	Dose of regeneration agent (eq/dm³ of ion exchange resin)	Compound formed	Concentration of regeneration effluent (percentage by volume and weight)		Volume of regeneration effluent (bed volumes)	Ion exchange capacity (eq/dm³ of ion exchange resin)	Volume of decationized wastewater (bed volumes)
			before neutralization with gaseous ammonia	after neutralization with gaseous ammonia			
1	2	3	4	5	6	7	8
HNO_3	1.46	NH_4NO_3	17.9	24.5	0.450	1.150	$1.150/C_{NH_4}^*$

2. Regeneration of cation exchange bed (Amberlite 200) with 50% H_2SO_4

1	2	3	4	5	6	7	8
H_2SO_4	1.46	$(NH_4)_2SO_4$	12.6	18.4	0.445	0.950	$0.950/C_{NH_4}$

* C_{NH_4} – concentration of ammonium ions in raw wastewater (as eq/dm³).

3.2. RECOVERY OF WATER AND CHEMICALS IN PROCESSING OF ACTIVE METAL OXIDES

One of the operations during processing of active metal oxides is digestion of metals (for instance zinc) or their oxides with the solution of nitric acid. The obtained solution is, after dilution with demineralized water, treated with sodium hydroxide for precipitation of metal hydroxide. The precipitated sludge is separated from the mother liquor, for example, by means of filtration. The filtrate (wastewater) contains ionic pollutants including the ions of toxic heavy metals. For example a filtrate from processing of active zinc oxide (wastewater) contains about 100 mg of zinc ions/dm^3 and 2,000-3,000 mg of sodium nitrate/dm^3. Thus it must be purified.

The method presented in fig. 6 allows to remove dangerous wastewater generated during processing of active metal oxides by directing the filtrate onto a chelate ion exchange bed,

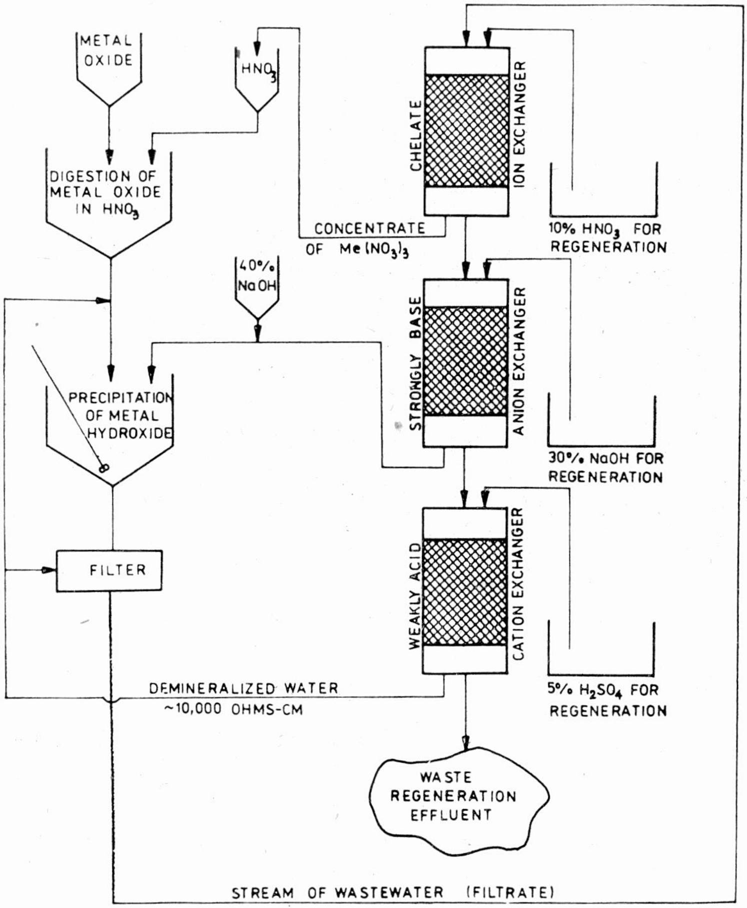

Fig. 6. Recycling of all constituents of wastewater from processing of active metal oxides to technological process by ion exchange method

Rys. 6. Jonitowa metoda zawracania wszystkich składników ściekowych z produkcji aktywnych tlenków metali do procesu technologicznego

where heavy metal ions (zinc ions) are sorbed. Thereupon the effluent is directed onto a strongly basic anion exchange bed, where anions are sorbed. A part of the effluent is used for preparation of sodium hydroxide solution. Another part is directed onto a weakly acid cation exchange bed, where the cations are sorbed to yield demineralized water. The latter is used for dilution of metal nitrate solution (before precipitation of metal hydroxide).

The chelate ion exchange bed is regenerated with concentrated solution of nitric acid. The regeneration effluent (which contains excess of nitric acid) is mixed with the solution of nitric acid used for digestion. In this way metal ions are recycled to production process.

The strongly basic anion exchanger bed is regenerated with concentrated solution of sodium hydroxide. The regeneration effluent is processed to sodium nitrate (the valuable fertilizer used in gardening).

The weakly acid cation exchanger bed is regenerated with 5% solution of sulphuric acid. The regeneration effluent, after neutralization with lime, is discharged to the sewer.

3.3. RECYCLING OF CHROMATES AND WATER FROM PLATING WASTEWATER TO PRODUCTION

The main source of wastewater of plating plants is rinsing water from rinsing of chromed or passived metal elements. Such wastewater contains about 200 mg Cr^{+6}/dm^3 and some amounts of metal ions.

The ion exchange method for recovery of water and chromates and their use for technological purposes is presented in fig. 7. The wastewater is directed at first onto a filter to remove suspended matter, then it is directed onto a strongly acid ion exchange bed where cations are sorbed. The decationized wastewater is directed onto a weakly basic ion exchange bed where chromic acids are sorbed. The demineralized water, the specific resistance of which is about 20,000 ohms-cm, is recycled to rinsing of metal elements.

The cation exchange bed is regenerated with a 50% sulphuric acid. The regeneration effluent after neutralization with lime is discharged to the sewer. The weakely basic anion exchange bed is regenerated with a 30% solution of sodium hydroxide. The regeneration effluent (sodium chromate concentrate) is immediately refilling the plating bath if the latter contains sodium chromate. If, however, it contains chromic anhydride (CrO_3) the regeneration effluent has to be decationized before recycling to such a bath. To this end, the regeneration effluent from the weakly basic anion exchanger bed is directed onto a strongly acid cation exchange bed, where sodium chromate is converted into chronic acids, which are recycled to the plating bath.

The strongly acid cation exchange bed is regenerated with a 5% solution of sulphuric acid and the regeneration effluent obtained is discharged to the sewer. The typical technological parameters are given in tab. 3.

4. SUMMARY

Concentrated solutions of mineral acids and sodium hydroxide or solution of ammonia are used in all technologies described. In this way the concentration of regeneration effluents can be increased to the level which allows their recycling to technology.

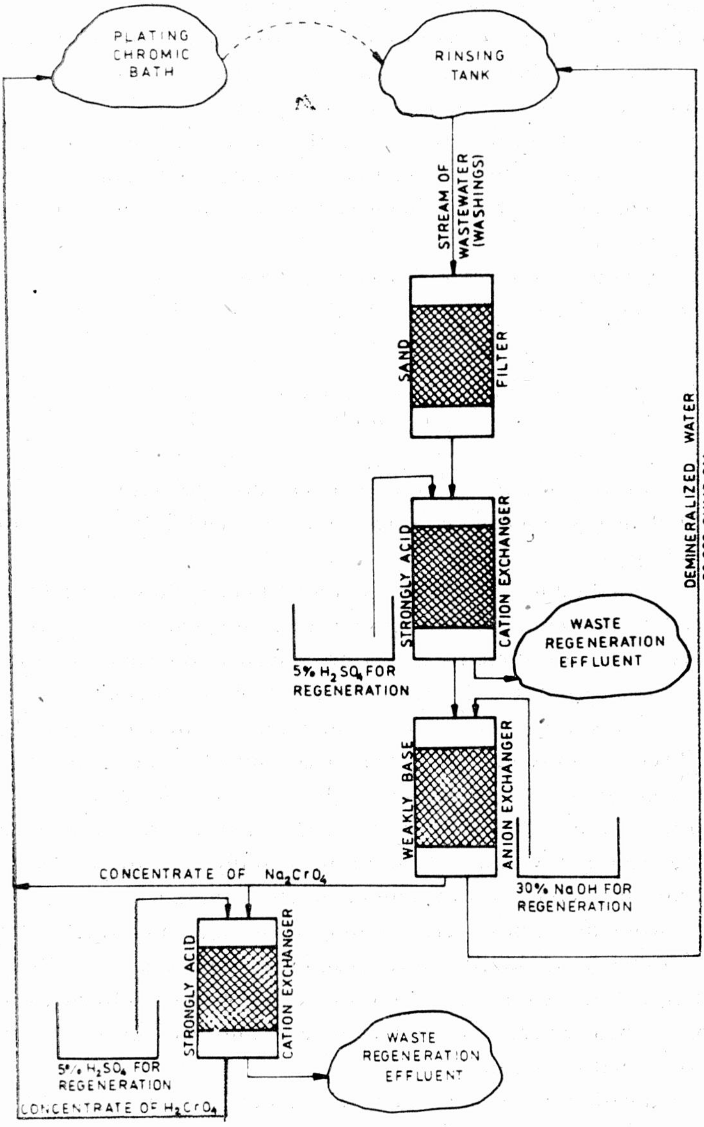

Fig. 7. Recycling of water and chromates or chromic acids from wastewater of plating plant effluent to technological process by ion exchange method

Rys. 7. Jonitowa metoda zawracania chromianów lub kwasu chromowego i wody z galwanizerskich ścieków chromowych do procesu technologicznego

Ion exchange methods: recycling of water ammonia and nitrates from ammonium nitrate processing wastewater, recovery of water ammonia from ammonia processing wastewater and recovery of water and chromates or chromic acids from plating plant

Table 3

Technological parameters typical of ion exchange method for recycling water and chromates from plating plant effluent

Typowe parametry technologiczne metody wymiany jonowej w recyrkulacji wody i chromianów, które pochodzą ze ścieków galwanizernii

1. Regeneration of weakly base anion exchanger with 30% NaOH

Regeneration agent	Dose of regeneration agent (g/dm^3 of ion exchange resin)	Compound formed	Concentration of regeneration effluent (percentage by volume and weight)	Volume of regeneration effluent (bed volumes)	Ion exchange capacity ($g\ Cr^{+6}/dm^3$ of ion exchange resin)	Volume of decationized wastewater (bed volumes)
1	2	3	4	5	6	7
NaOH	72.5	Na_2CrO_4	18.7	0.785	39.8	$39.8/C^*_{Cr+6}$

2. Decationization of regeneration effluent from weakly base anion exchanger bed

1	2	3	4	5	6	7
—	—	CrO_3	9.5	0.895	—	—

* C_{Cr+6} — concentration of chromate ions in deanionized wastewater (as g/dm^3).

effluents have been tested on pilot plant scale. However, the recovery of wastewater constituents from active metal oxides processing has been tested only on a laboratory scale.

Generally speaking, the principles of the method presented in this paper may be used in design of treatment method for other kinds of wastewater.

METODA WYMIANY JONOWEJ W RECYRKULACJI WODY I SKŁADNIKÓW ŚCIEKOWYCH

W pracy przedstawiono ogólne zasady recyrkulacji domieszek ścieków do procesu technologicznego. Szczegółowo przedstawiono jonitowe metody recyrkulacji amoniaku, azotanów i wody ze ścieków z produkcji azotanu amonu; recyrkulacji amoniaku i wody ze ścieków z produkcji amoniaku; wody i chromianów lub kwasów chromowych ze ścieków galwanizerskich; chemikaliów i wody ze ścieków z produkcji aktywnych tlenków metali.

W metodach tych do regeneracji kationitów zastosowano 50% kwas siarkowy lub azotowy, a do regeneracji anionitów — 30% roztwór wodorotlenku sodowego lub 20% roztwór amoniaku. Pozwoliło to na otrzymanie roztworu poregeneracyjnego o stężeniu umożliwiającym jego bezpośrednią recyrkulację do procesu technologicznego.

DAS IONENAUSTAUSCHVERFAHREN IN DER RÜCKFÜHRUNG DES WASSERS UND DER ABWASSERINHALTSSTOFFE

Im Bericht werden allgemeine Richtlinien der Rezirkulation in der Abwassertechnik erörtert. Eingehend wird das Ionenaustauschverfahren zur Rückführung: des Ammoniaks, der Nitrate und des Wassers aus Abwässern die bei der Herstellung von Ammoniumnitrat entstehen; des Ammoniaks und des Wassers aus der Ammoniakproduktion; des Wassers und der Chromate bzw. der Chromsäuren aus den Galvanikabwässern, sowie der Chemikalien und des Wassers aus den Abwässern die bei der Produktion von aktiven Metalloxyden entstehen.

Zur Regeneration der Kationenaustauschern wurde eine 50% Schwefelbzw. Salpetersäure verwendet. Zur Anionenaustauschern eine 30%-ge Natriumhydroxydlösung oder 20%-ige Ammoniaklösung. Gewonnen wurde eine. Regeneratlösung, deren Konzentration die unmittelbare Rückführung in die Verfahrenskette ermöglichte.

МЕТОД ИОННОГО ОБМЕНА В РЕЦИРКУЛЯЦИИ ВОДЫ И СТОЧНЫХ ВОД

В работе представлены общие принципы рециркуляции сточных компонентов в технологию. Кроме того, подробно обсуждены ионитные методы рециркуляции аммиака, нитратов и воды из сточных вод от производства нитрата аммония; рециркуляции аммиака и воды из сточных вод от производства аммиака; воды и хроматов или хромовой кислоты из сточных вод от гальванических цехов; химикалий и воды из сточных вод от произдвоства активных окисей металлов.

В этих методах для регенерации катионов была применена 50% серная или азотная кислота, а для регенерации анионитов — 30% раствор гидроокиси натрия или 20% раствор аммиака. Это позволило получить послерегенерационный раствор с концентрацией, дающей возможностсь непосредственной рециркуляции в технологию.