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The current state of the problem of the elimination of boron from waste waters

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ABSTRACT. The advances in the extraction of boron-containing substances from waste waters and natural brines are examined and surveyed. The current prospects for the solution of the problem of creating an ecologically clean technology for the purification of industrial liquid waste with recovery of valuable components are described. The results of studies on the problem, obtained under experimental and industrial conditions, are discussed.

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I. Introduction

The disturbance of ecological equilibria in the biosphere has raised at the present time a series of fairly acute questions associated with the protection of the environment, which necessitates more stringent requirements as regards the protection of water, soil, and the atmosphere. The requirements have become more stringent both as regards the purity of the liquid waste discarded into water-containing areas and their amount.

The industrial waters, sludge, and mother liquors in modern factories processing boron-containing raw material contain an appreciable quantity of boron. This fact poses a serious problem in many industries concerning the extraction and utilisation of boron-containing products.

The use of modern methods for the extraction of boron from waste waters makes it possible to improve the technological processes and to solve problems of the recovery of boron and of the preservation of natural resources.

In nature, boron is encountered in the form of more than 80 independent materials. In the dissolved state in water, boron is present as salts of boric and polyboric acids and also as free orthoboric acid.

The data concerning the toxicity of boron compounds are fairly contradictory and the toxicities of many boron-containing substances have been hardly investigated. Soluble boron compounds are classified as polytropic poisons, prolonged action of which can induce chronic intoxification and diseases of the nervous system.

The limiting permissible concentrations (LPC) in water-containing areas used in fish farming are 0.1 mg litre^{-1} in terms of B_2O_3 and 0.017 mg litre^{-1} in terms of boron and in sanitary-domestic water it is 0.5 mg litre^{-1} in terms of boron. A norm for the LPC of boron in drinking water has not been laid down, but a concentration of 1 mg litre^{-1} has been recommended in the USA.

Thus the current interest in the problem of the extraction of boron from waste waters is associated, among others, with economic problems and the protection of human health.

The methods for the processing of natural types of boron-containing raw material involve a series of a wide variety of technologies for the extraction of boron from aqueous solutions, such as precipitation of boron in the form of sparingly soluble compounds, coprecipitation, extraction with organic solvents, sorption on selective sorbents, separation by electro-ion-exchanger membranes, etc. These methods are at present being developed.

II. Reagent methods for the extraction of boron from waste waters

The reagent methods for the purification of waste waters are based on the precipitation of boron in the form of sparingly soluble compounds and are fairly effective in the case of high concentrations of boron-containing substances in the treated liquid waste.

Treatment of the waste waters obtained in the processing of boron-containing raw material with lime water makes it possible to reduce appreciably and stabilise the concentration of boron. In this case it is possible to reduce the concentration of boron trioxide from 2.5–2.7 to 0.20–0.25%. When lime water is added, calcium borate crystallises from boron-containing solutions. The composition of the borate $x\mathrm{CaO}.y\mathrm{B_2O_3}.z\mathrm{H_2O}$ depends on the precipitation conditions. Thus borates with the ratios $x:y:z$ = 2:3:13 and 1:1:6 are formed at 25 °C, borates with the ratios 2:3:9 and 1:1:4 are formed at 80 °C,[1–3] while at 95 °C borates with the ratios 2:1:1, 2:3:7, and 1:3:5, and, after the introduction of a seed, also 4:5:7, 2:3:5, and 2:7:8 were isolated.[4] From the standpoint of subsequent use, calcium diborate hexahydrate $\mathrm{CaO}.\mathrm{B_2O_3}.6\mathrm{H_2O}$ (1:1:6) is of greatest interest. The borate is preciptiated via the reaction:

$$2\mathrm{H_3BO_3} + \mathrm{Ca(OH)_2} + \mathrm{aq} \rightarrow \mathrm{CaO}\cdot\mathrm{B_2O_3}\cdot n\mathrm{H_2O} + \mathrm{aq}.$$

It is essential to note that the precipitation process is influenced significantly by the temperature, the amount of lime water, and the pH.[5,6] In order to obtain the borate with the 1:1:6 composition, it is essential that the temperature should be not higher than 25–30 °C. The optimum temperature is 22–27 °C. In order to obtain a borate with a stable composition and involving the maximum extraction of boron from the solution, the pH of the reaction medium should be in the range 11.4 ± 0.20.[3] Furthermore, it has been found that the range of grain sizes and the chemical composition of calcium diborate depend on the content of impurities in the solution being purified and in the lime water. The purification of the lime water should ensure the content of the inadequately slaked component not greater than 0.2% and 0.015% Fe_2O_3 for an overall 10% content of active CaO.

In the course of the precipitation of the 1:1:6 borate, a small amount of amorphous variable-compositon calcium borate is produced. The amount of B_2O_3 in the amorphous component of the precipitate is relatively constant and the B_2O_3:CaO weight ratio is in the range 0.85–1.05. In the crystalline product, this ratio is always close to the theoretical value of 1.24.[6] The yield of the boron obtained in the amorphous phase is up to 10–15% of its content in the solution.

In the course of the preparation of commercial calcium diborate, the crystal growth stage is rate-limiting, the maximum size of the crystals not exceeding as a rule 50 μm. The concentration of boron oxide in the liquid phase diminishes from 1.5 to 0.15–0.17% after mixing the reactants for 1–3 min at 25 °C, i.e. it is reduced virtually to the equilibrium value.

It is notable that, in the purification of waste waters with a high B_2O_3 content, the precipitate contains, other conditions being equal, a greater amount of the crystalline phase. A similar effect has been obtained also in the presence of a definite amount of a seed in the reactor.

A reactor design ensuring the separation of finely disperse impurities from the crystalline phase during the synthesis of calcium diborate has been developed.[4] The yield of the commercial borate is in this case 96.8 ± 0.5%, the calcium borate being homogeneous in its chemical composition and in terms of its grain size.

The presence of boron-containing kerosene and polyacrylamide (PAA) hydrocarbons in waste waters does not affect the efficiency of the extraction of boric acid.[7] However, the crystals of calcium borate preciptiated from a solution containing these organic impurities are acicular in shape and a tendency towards the agglomeration of the crystals and loss of the regular form corresponding to the internal structure of the crystal is observed. This can be accounted for by the fact that the impurities influence the crystallisation process through a change in the structure of the solution and through adsorption on the faces of the crystals, inducing a change in the rate of their growth.

The coprecipitation of calcium and copper borates makes it possible to isolate up to 93–95% of boron from a solution containing 0.2–0.4% B_2O_3. After preciptiation, the solution contains 0.03% B_2O_3 and the precipitate contains 22.4% B_2O_3, 18.3% CuO, 36.3% CaO, and 23.1% H_2O. Somewhat poorer results are obtained in the coprecipitation of calcium borate with other microimpurities—manganese and cobalt.[8]

A decrease in the content of boric acid in the water being purified can be achieved by isolating at 95 °C dicalcium borate $2CaO.B_2O_3.H_2O$, the solubility of which is low. For this purpose, waste waters containing up to 0.25% B_2O_3 are treated with lime water, the measured amount of the latter, recalculated in terms of CaO, amounting to 130–170% of the stoichiometric amount[9] according to the reaction equation:

$$2Ca(OH)_2+2H_3BO_3=2CaO\cdot B_2O_3\cdot H_2O+4H_2O.$$

The residual content of B_2O_3 in the waste water is 0.03–0.04%.

It is essential to note that the extraction of boron from waste water by precipitating sparingly soluble calcium borate is widely used on the industrial scale.

The mother liquors in the boric acid industry, containing 1.3–1.6% B_2O_3, 21–23% $MgSO_4$, and 0.2–0.6% H_2SO_4, are also treated with magnesium oxide.[10] In this case, magnesium borates having the composition $xB_2O_3.yMgO.zH_2O$ are precipitated. At 95 °C, for a MgO norm amounting to 4.5 mol per mole of B_2O_3 and for a stirring time of 2 h, more than 90% of the boron is precipitated and the filtrate contains 0.26% B_2O_3 after separating the precipitate. Treatment of the mother liquors with ammonia and carbon dioxide or ammonium carbonate makes it possible to obtain ammonium borosulphate and magnesia:

$$4H_3BO_3+(NH_4)_2CO_3=(NH_4)_2B_4O_7+CO_2+6H_2O,$$

$$4MgSO_4+4(NH_4)_2CO_3+10H_2O=$$

$$=3MgCO_3Mg(OH)_2\cdot 9H_2O+4(NH_4)_2SO_4+CO_2.$$

The precipitated magnesium carbonate is separated from the solution and the latter is neutralised with H_2SO_4 and dried, which affords ammonium borosulphate containing 6% B_2O_3, 70% $(NH_4)_2SO_4$, and 20% $MgSO_4$.

It is essential to note that the magnesium and manganese borate precipitates can be used to prepare boric acid. Calcium borate is employed as a substitute for boric acid in many chemical processes. It has also been suggested that the precipitate, formed when boron-containing waste waters having the composition 7% B, 15% B_4C, 60% B_2O_3, and 18% of carbon black are allowed to stand, be subjected to a high-temperature treatment in order to obtain boron carbide.[7]

Waste waters containing 40–50 g litre^{-1} of boric acid can be used in the manufacture of boron dyes.[11] For this purpose, they are treated with sodium carbonate in an amount necessary for the formation of the tetraborate:

$$4H_3BO_3+Na_2CO_3=Na_2B_4O_7+CO_2+6H_2O,$$

and for the formation of a product in which the ratio $Na_2CO_3:Na_2B_4O_7.10H_2O$ does not exceed 10.

In aqueous solutions, boric acid forms complexes with tartaric and trihydroxyglutaric acids. Thus boron can be isolated from very dilute solutions by precipitation in the form of salts with these acids.[12]

The methods for the extraction of boron from waste waters by precipitating sparingly soluble borates are fairly simple to apply and are widely used on the industrial scale. However, the use of these methods is justified in weakly mineralised systems in which the concentration of B_2O_3 is at least 0.3–0.5%. The presence of alkali metal chlorides and sulphates in the solution lowers the qualitative parameters of the process. One of the deficiencies of the method is the impossibility of attaining a high degree of elimination of boric acid from the liquid waste.

III. Extraction of boron from aqueous solutions on inorganic sorbents

On precipitation of certain metal hydroxides from aqueous solutions, boron ions are entrained to some extent. Coprecipitation is explained by the formation of the corresponding metal borates.

The limits of the practical applicability of the given method are between 1 and 3 g litre^{-1} in terms of B_2O_3. The upper limit is set by the duration of the protecting effect of the sorbent and the lower by the formation of eluates dilute in boron on regeneration of the sorbent, which hinders the extraction of boron from them on further treatment.

The sorbents employed are the alkali metal hydroxides $Al(OH)_3$, $Fe(OH)_3$, $Sn(OH)_4$, $Ti(OH)_4$, $Mn(OH)_4$, $Ni(OH)_2$, $Mg(OH)_2$, and $Zn(OH)_2$.[13–16] The degree of coprecipitation of boron with these hydroxides increases with enhancement of their basic properties. Thus, at a boron concentration of 0.31 g litre^{-1}, the amounts of boron coprecipitated are 90% by $Ni(OH)_2$, 60% by $Mg(OH)_2$, $Al(OH)_3$, and $Fe(OH)_3$, and 25% by $Zn(OH)_2$. This suggested the following exchange mechanism: borate ions$\rightleftarrows OH^-$ ions of the hydroxides. However, $Zn(OH)_2$ sorbs much less boron than had been suggested and $Cu(OH)_2$ does not sorb it at all. This can be accounted for by the occurrence, together with ion exchange, of a chemical interaction involving the formation of borates, which is confirmed by studying the influence of the concentration of borate ions on the sorption of boric acid. When the boron concentration in solution was altered from 0.31 to 31 g litre^{-1}, the amount of boron coprecipitated changed from 0.037 to 0.806 g litre^{-1} for $Zr(OH)_4$ and from 0.099 to 3.534 g litre^{-1} for $Ni(OH)_2$. The IR spectra of the hydroxides precipitated from boric acid solutions at different concentrations permit the conclusion that the interaction of a nickel salt with boric acid involves the formation of nickel borate, which is coprecipitated together with $Ni(OH)_2$, the structure of the borate resembling that of ulexite $CaNa[B_5O_6(OH)_6].5H_2O$, while in the case of the hydroxides $Al(OH)_3$ and $Zr(OH)_4$ ion exchange takes place.

Data have been published[5,6] concerning the preparation of borate concentrates from petroleum waters (0.25–0.46 g litre^{-1} in terms of B_2O_3) with the aid of $Mg(OH)_2$, MgO, and heat-treated dolomite ($MgCO_3$ + $CaCO_3$). When boron was extracted with magnesium hydroxide, the sorption capacity was 0.3% in terms of B_2O_3, which is of virtually no practical interest. Using magnesium oxide and heat-treated dolomite as sorbents under static conditions with a sorbent : solution ratio of 1 : 100 and for 8 h contact, it is possible to extract 50–70% of B_2O_3, the degree of extraction being independent of the degree of mineralisation of the brines. Under dynamic conditions, it is possible to achieve almost complete extraction of boron (up to a residual content of 20 mg litre^{-1} of B_2O_3). However, the cost of magnesium oxide is fairly high and it is therefore desirable to use heat-treated dolomite. The process parameters have been established:[17] ratio of solid and liquid phases S : L = 1 : 100, temperature 30–45 °C, pH 9. Under these conditions, the degree of elimination of boron is 90%.

A method has been developed for the elimination of boron from highly mineralised natural solutions,[18] involving their treatment with chromium hydroxide in an amount of 2–12 g per 100 ml of the solution at pH 8.5. The sorbent is supplied in two lots in equal portions, after which the solution is stirred for 30 min. For a settling time of the suspension of 30 min, the efficiency of the extraction of boron reaches 65%. The nature of the anion in the initial chromium salt and its concentration have almost no effect on the extraction of boron in the pH range 6.8–12.[19]

A sorbent consisting of granulated magnesium-nickel hydroxide (MNH) has been synthesised.[20] Its comparison with zirconium hydroxide shows that under static conditions the rates of equilibration on the MNH sorbent are almost twice as high but the capacity of the zirconium hydroxide is greater. The experiments carried out under dynamic conditions shows that, in the sorption of boron from concentrated brines, preference should be given to zirconium hydroxide.

A technology has been developed for the extraction of boron by a sorbent based on zirconium and magnesium-nickel hydroxides, involving a multicycle procedure, in which the solutions are brought into contact with the sorbent, the sorbent is regenerated with an alkaline solution, and boron is isolated from the eluates by means of compounds of univalent or divalent metals with formation of sparingly soluble borates and the mother liquor.[21] The mother liquor from the preceding cycle is brought into contact with the sorbent before its regeneration in the next cycle.

Zirconium hydroxide, obtained directly in the boron-containing solutions, was proposed as the sorbent.[23] This hydroxide gives rise to a fairly high degree of precipitation of boron. Thus, after a fourfold precipitation, the degree of extraction of boron from a solution containing about 1 g litre^{-1} of B_2O_3 in 98.5%. The boron is extracted from the residue by being converted into borax with sodium hydroxide and by leaching the deposit with warm water. The sorption properties of granulated zirconium hydroxide (GZH) have also been investigated[23] by freezing and by the gel-sol methods. Boron was extracted from waste waters with an overall degree of mineralisation of 4.2 g litre^{-1} and a high concentration of boric acid at pH 5. The capacities of the sorbents obtained by the above procedures are 44.9 and 38.2 mg g^{-1} respectively.

Stable polynuclear derivatives of zirconium nitrate exhibit an enhanced ability to react with borates.[24] H_3BO_3 is sorbed under static conditions, the equilibration time being 30 min. The ratio of the solid and liquid phases is 1 : 30. For a H_3BO_3 content in the liquid waste between 0.5 and 2.5 g litre^{-1}, the percentage extraction of the acid is independent of its concentration. The greatest sorption effect is observed at pH 9 and reaches 90% in one cycle. It has been established that heating assists sorption.

Studies on the sorption of boron by granulated metal hydroxides from boric acid solutions and natural magnesium chloride brines under static conditions at boron concentrations between 0.05 and 0.25% in terms of B_2O_3 have shown that[25] the optimum sorption conditions are attained at pH 3.5–4.0 and temperatures in the range 35–40 °C. In terms of their equilibrium sorption capacity, the metal hydroxides can be arranged in the following sequence: Zr^{4+} (in NaCl solution) > Al^{3+} > Zr^{4+} > Fe^{3+}.

Zirconium hydroxide has the maximum capacity and this sorbent has been tested also under dynamic conditions. The maximum capacity is attained at a flow rate of the solution being purified of 0.2–0.5 ml min^{-1}, at 25–30 °C, and at pH 3.5–4.0.

According to Nikolaev's study,[26] the efficiency of the capture of boron from water by different hydroxides at pH 8.2–8.3 is characterised by the following sequence:

$$ZrO_2 > La_2O_3 > SiO_2 > TiO_2 > Fe_2O_3,\ Al_2O_3.$$

The presence of certain ions has a fairly appreciable influence on the extraction of boron by metal hydroxides. For example, the presence of sodium and lithium chlorides promotes an increase in the capacity of zinc, nickel, iron, aluminium, and tin hydroxides with respect to borate ions. This can be accounted for[27] by the influence

of the above electrolytes on the structure of the boron ions in solution. At the same time, the absorption borate ions diminishes in the presence of anions in the following sequence: $NO_3^- > Cl^- > SO_4^{2-}$. With increase in the boron concentration in the initial solution, the influence of anions diminishes appreciably.[28–32]

The extraction of boron by aluminium and iron hydroxides has been investigated in fair detail.[33] The concentration and nature of the hydroxides, the contact time, and the pH of the reaction medium were adopted as the principal factors governing the process. Aluminium hydroxide has been obtained by adding aluminium sulphate to a sample of the waste water and iron hydroxide was prepared by adding iron chloride. The maximum boron extraction effect is observed at pH 7.0–9.0 and is attained at the instant of the formation of the hydroxides, i.e. the separation of the suspension in order to extract the spent hydroxide is best performed in a contact clarifier or on a contact filter. With increase in the hydroxide concentration, the coprecipitation effect also increases, but such relations are not highly linear and the copreciptiation effect increases up to a certain limit.

The removal of boron from natural brines[34] is most effective when the Al_2O_3 sorbent is used in an amount corresponding to 0.5–20% relative to the mass of the brine. The suspension containing the sorbent is heated to 60–80 °C and stirred at this temperature for 30–60 min. The residual boron content in the brine is less than 50 mg litre^{-1} and the degree of extraction reaches 87–97%. The sorbent is separated from the solution by allowing it to settle, after which the boron is desorbed with a 10% mannitol solution. Solutions of glycerol, sorbitol, and a number of other substances can be used as desorbing agents. A procedure for the elimination of boron compounds from magnesium chloride brines with activated alumina or activated bauxite has been proposed.[55] When the ratio of the Al_2O_3 content to the mass of the brine is 1:4, the degree of purification is 91%.

Studies[36] on the sorption properties of the ash formed after the combustion of coal are of interest. Since the ash contains sodium, potassium, calcium, magnesium, aluminium, and iron ions, the hydroxides of the above metals are formed at elevated pH and bind the borate ions.

Thus we may note that the most effective inorganic sorbent is zirconium hydroxide, which, however, suffers from a serious deficency—low mechanical strength, which is an obstacle to its employment in industry. Aluminium hydroxide also exhibits a high efficiency in extracting boron.

The method involving the coprecipitation of boron with metal hydroxides makes it possible to attain high degrees of elimination of boron from waste water, but it is less critical as regards the content of dissolved alkali metal salts. However, one must add that the above method is technologically complex: the rates of filtration are low and a constant regeneration of the carrier deposit is required, which involves the consumption of acids and alkalies. The deposits as a rule contain boron at a low concentration, their composition is not constant, and they require additional processing. The process has not been applied widely on an industrial scale.

IV. Sorption of borate ions on anion-exchange resins

The methods for the extraction of boron with the aid of ion-exchange materials are applicable mainly to weakly mineralised aqueous solutions with a fairly low content of B_2O_3 (up to 2–3 g litre^{-1}).[9] The need to apply ion-exchange methods arises in the extensive purification of waste waters and also in the extraction of boron for analytical and chromatographic purposes and for the separation of isotopes.

The studies on the sorption properties[37,38] of anion-exchange resins of neutral and weakly basic types in relation to the extraction of boron from waste waters have shown that weakly basic anion-exchangers of the polycondensation type, containing hydroxy-groups as well as primary, secondary, and tertiary amino-groups, are more selective with respect to boron. Up to 80% of boron is extracted from pure solutions of boric acid containing 0.28% B_2O_3, but the attainment of this degree of purification requires a long contact time.

The presence of metal salts in the solutions lowers the degree of extraction of boron. This fact as well as the low exchange capacity of the sorbents suggest that mixed and highly basic sorbents may be more promising, but these do not exhibit selectivity with respect to borate ions.

There are insufficient literature data and recommendations concerning the application of USSR-produced ion exchangers. For example, the AV-17 anion-exchange resin has been suggested for the isolation of boric acid from heat exchangers, aqueous salt solutions, and waste waters.[39–42] The AV-17 anion-exchange resin in the OH-form has been used for the extraction of boron from heat exchangers of the power reactor of an atomic power station.[43] The degree of purification reached 99.5% and the dynamic capacity of the resin was 100–120 g litre^{-1}. It has been established[44] that, with increase in the concentration of boric acid by a factor of 10, the degree of sorption of boron increases by a factor of 2–4, while a temperature rise from 18 to 50 °C lowers the degree of extraction of boron, especially for dilute solutions. The resin is regenerated with a potassium hydroxide solution and the eluate is treated in an electrodialysis cell with cation-exchange and dipolar membranes, which results in the extraction of 98% of borate ions.

The sorption capacity of the AV-29 anion-exchange resin with respect to boron is 507 mg litre^{-1} when the resin comes into contact with a solution whose pH is 6.[45] Compared with the AV-17 anion-exchange resin the efficiency of the AV-29 resin is higher by a factor of 1.7.

According to the data of Samberskii, et al.,[46] the capacity with respect to boron increases in the following sequence of anion-exchange resins: AV-17 × 8, AV-29, AN-2F, EDE-10P, AN-31, i.e. with increase in the content of hydroxy-groups in the resin. In the presence of salts, the capacity of the sorbents falls sharply (especially that of the AV-17 anion-exchange resin) owing to the high ion-exchange affinity for the Cl^- and SO_4^{2-} ions. The influence of cations on the sorption of boron diminishes in the sequence $K^+ > Na^+ > Zn^{2+} > Mg^{2+}$, which is apparently caused by the different capacities of the cations for hydration. Thus the presence of even small amounts of NaCl and $ZnCl_2$ diminishes sharply the capacity of the resins with respect to boron.

The complex-forming sorbents ANB-11 and ANB-11m are highly effective in the extraction of boron from mineralised waters.[47,48] The static capacity of the above anion exchangers is 80 mg litre^{-1} and the optimum pH at which the boron-containing waters and the sorbents are brought into contact is 7. The presence of salts hardly affects the sorption process. Sorbents distinguished by a satisfactory kinetic parameter, which are readily regenerated with HCl, have undergone industrial tests.[49] In order to increase the degree of purification, the sorption is carried out on anion-exchange resins subjected to preliminary treatment with methanol.

Studies directed towards the search for ion-exchange materials selective with respect to borate ions are of practical interest.

In order to increase the sorption capacity with respect to boron, anion exchangers of the aminoepoxide type have been modified chemically which increased the concentration of hydroxy-groups.[50] Anion exchangers of the aminoepoxide type[51] and the epoxyamino-type, B-8, B-257,[52] and SB-1[53] have been obtained in this way. The experimental data for the extraction of boron from natural concentrated magnesium chloride brines, obtained under static conditions, showed that B_2O_3 concentrations in excess of 1 g litre^{-1} and a solution temperature of 40 °C are optimum for the sorption of boron. The equilibrium capacity of ion exchangers under these conditions is 110 mg h^{-1}. However, at a B_2O_3 concentration below 1 g litre^{-1}, the sorbent capacity falls sharply and the ion-exchange purification becomes inefficient.

For example, the SB-1 ion-exchange resin, containing in its structure hydroxy- and amino-groups which are selective with respect to boron, can be used for the effective extraction of boron from solutions at a concentration of 2–3 g litre^{-1} of B_2O_3, but, owing to the instability of the borate ions, boron cannot be extracted as far as the limiting permissible concentrations (LPC). The study of the pH dependence of the sorbent capacity with respect to boron showed that the maximum occurs at pH 7.4–8.8 and the total dynamic exchange capacity of the resin is 160 mg of B_2O_3 per gram of the resin. The degree of extraction of boron is 82% for an initial B_2O_3 content of 1.2–3.22 g litre^{-1}.[54] When the SB-1 ion-exchange resin is compared with the zirconium-hydroxide based inorganic sorbent GZH, whose properties were discussed in the previous Section, it is noteworthy that the latter sorbent permits a more extensive purification of the solutions, while the SB-1 sorbent has a higher mechanical strength by an order of magnitude.[55] The equilibrium pH depends on the content of salts in the solution. In the presence of a high salt content, the sorption pH differs from the initial value by more than 1–2 units, while in the presence of a low salt content the pH is 8.5–9.5, which is attributed to the "buffer" capacity of the impurities.

Resins with active catechol groups exhibit a fairly high capacity with respect to borate ions. On this basis, the ANPK-31 sorbent has been synthesised. It consists of the AP-31 anion-exchange resin modified with catechol.[56] At pH 7.5, this resin extracts 60 mg of boron per gram of the resin.

A technology has been developed for the preparation of a sorbent.[57] It is based on the use of chitosan (a chitin hydrolysis product), which is a glucosamine polysaccharide. Fe_3O_4 grains coated by the chitosan solution bind boron into complexes with chitosan. The efficiency of the purification is 70%. This method of purification has been validated by industrial tests.

The interaction of boric acid with polyhydroxy-compounds, which include aliphatic and cyclic diols and triols and polyhydric alcohols and phenols, has been fairly thoroughly investigated hitherto. One of the sorbents exhibiting a high selectivity is poly(vinylene glycol) (PVG),[58] which is a linear insoluble powdered polymer. Its capacity is 91.4 mg of B_2O_3 per gram of the sorbent, an increase in the pH of the solution from 3.5 to 8.5 increasing the degree of extraction of boron. An increase in the content of alkali metal and magnesium salts also improves the sorption of boric ions. However, PVG has not come to be widely used owing to its operating properties and also because it is impossible to obtain concentrated solutions in the desorption process.

Much attention has been devoted to the preparation of polymerised sorbents with aminopolyol groups capable of extracting selectively boron compounds from aqueous solutions at B_2O_3 concentrations from 0.5 to 1 g litre^{-1} and above.[59] An example of such a sorbent is the Amberlite XE-243 resin, which exhibits a high selectivity with respect to boron in neutral and alkaline media. In an acid medium, the resin capacity falls sharply. These capacities are 1.74, 1.5, and 0.7 mequiv. litre^{-1} respectively. The presence of NaCl and $MgCl_2$ does not affect the efficiency of the process, which is carried out in weakly alkaline medium. The resin has been recommended for the extraction of borates from natural brines.

Sorbents have been synthesised using tris(hydroxymethyl)amino-methane as the aminopolyl.[60] The capacity of these sorbents reaches about 70 mg of H_3BO_3 per gram of the resin for sorption from solutions containing 1 g litre^{-1} of boric acid and 50 mg per gram of the resin for sorption from solutions with a high solvent content. The optimum sorption pH is 7. The presence of salt hardly affects the capacity of the sorbents with respect to boron, so that it is useful to use them for the extraction of boron from solutions against a strong salt background. The character of the interaction of borate ions with the sorbent based on *N*-methylglucosamine is similar. However, when these sorbents are used in chloroform, the sorption maximum shifts to a more alkaline region. The resins are readily regenerated with hydrochloric acid and less effectively with hard water and alkali. The sorption process takes place less effectively in the presence of magnesium sulphate. The presence of $MgCl_2$ increases the capacity of the resin with respect to boron which is apparently associated with the salting-out of boron into the sorbent phase. The presence of NaCl, KCl, and LiCl hardly affects the resin capacity. It has been established that the process kinetics depend very significantly on the boric acid concentration in the solution.

It is noteworthy that the capacities of all the sorbents based on phenol-containing resins are lower than those of Amberlite XE-243 and its analogues. The optimum complex-forming sorbent is the resin based on *N*-methylglucosamine. Furthermore, a major advantage of polymerisation sorbents compared with the poly-condensation phenol-containing resins is their high chemical stability.

The suggestion that an activated charcoal impregnated with the Methylene Blue dye be used for the purification of boron-containing waste waters is of interest.[61–63] A fairly high efficiency of the purification of boron-containing waste waters has been achieved using Filtrasorb activated charcoal. The degree of purification was 90% for an initial boron concentration of 5–30 mg litre^{-1}.

The extraction of boron with a mixture of organic and inorganic sorbents merits attention.[64] The method involves the treatment of the anion-exchanger with a solution of zirconium oxalate and then with ammonia at pH 9–10. The sorbents prepared on the basis of the AV-17–12P, AN-2F, and PD7-10G anion-exchange resins are fairly effective in the removal of boron-containing substances from water (65%). However, the technology of their preparation is complex.

Thus one may conclude that the sorption method has a number of evident advantages and permits a fairly extensive purification of the solution without its secondary contamination. The disadvantages of the sorption technology, which complicates its practical application, are the absence of the industrial production of sorbents with the required qualities, low rates of sorption, and low economic parameters of the process.

V. Extraction of boron with organic solvents

The extraction of boron with organic solvents is one of the highly effective and selective procedures. Studies have shown that the most effective extractants for borate ions are hydroxylated organic

compounds. In the general case, the greater the number of hydroxy-groups in the structure of the organic substance, the greater its efficiency. The concentration of hydroxy-groups can be increased either by diminishing the molecular weight of monohydric alochols or by increasing the number of hydroxy-groups in the molecule by going over to polyols. As a consequence of this, two main trends have arisen in the study of the extraction of boron—extraction with monohydric and polyhydric alcohols.

Studies on a series of alcohols have shown that the efficiency of the extraction of boron with alcohols falls with increase in their moelcular weight. In terms of decreasing efficiency of the extraction of boron by alcohols, the latter can be arranged in the following sequence: 1-butanol, isobutyl alcohol, 1-pentanol, isopentyl alcohol,..., 1-octanol,..., isododecyl alcohol.

With increase in the concentration of the salting-out agent, for example $MgCl_2$, in the aqueous phase, the above sequence is in general retained, but alcohols with the iso-structure become much more effective than the alcohols with the normal structure. In concentrated $MgCl_2$ solutions, the efficiency of the alcohols with a branched structure then increases with increase in the length of the carbon chain. The alcohol efficiency sequence changes: iso-octyl alcohol,..., isopentyl alcohol, isobutyl alcohol, 1-pentanol, 1-butanol, 1-nonanol.

Thus, in the extraction of boron from bischofite brines, the most effective organic extractants are iso-octyl and isopentyl alcohols. In order to increase the efficiency of the isolation of boron, a mixture of several organic compounds is frequently used. For example, a boron extractant consisting of a mixture of aliphatic alchols (60–70% of isopentyl alcohol, 20–25% of isobutyl alcohol, and 5–10% of propylbutyl alcohol) has been proposed[65] for the extraction of boric acid. The extractant is selective with respect to boron and is immiscible with water. The maximum degree of extraction of boron is 99% and it can be attained for a boron content in the initial solution of 1 g litre^{-1}.

Table 1. The partition coefficients of boric acid in extraction with 2-substituted β-diols.

No of extractant	K_p		
	pure boric acid solution	boric acid solution saturated with NaCl	boric acid solution saturated with $MgCl_2$
(I)	13.8	39	14.9
(II)	14.6	–	58
(III)	20	40	30
(IV)	31	42	–
(V)	30	37	53

A fair amount of attention is being devoted to studies on the extraction of boric acid from aqueous solutions of diols. A fairly high degree of extraction of boron is attained[66] using 2-propylheptane-1,3-diol (I), 2-butyloctane-1,3-diol (II), 2-isopropyl-6-methylhexane-1,3-diol (III), 2,2,4-trimethylpentane-1,3-diol (IV), and 2,2,5-trimethylhexane-1,3-diol (V).

The best diluents for extractants (I) and (II) are chlorohydrocarbons, toluene, (kerosene can also be used), while the best diluent for extractants (IV) and (V) is chloroform. Table 1 presents the equilibrium partition coefficients K_p of boric acid in extraction with 0.5 M solutions of extractants (I)–(V) in chloroform for a 0.1 M solution of boric acid without electrolytes and against the background of saturated sodium and magnesium chloride brines at 20 °C. With increase in the extractant concentration in the diluent, the degree of extraction rises. The maximum partititon coefficient is observed for a tenfold molar excess of the extractant. A decrease in the boric acid concentration in the solution extracted to 0.31 g litre^{-1} does not diminish the degree of extraction when extractants (I)–(IV) are used, but the degree of extraction falls somewhat (from 96.78 to 90.26%) in the case of extractant (V). The extractants investigated extract boric acid over a wide pH range. However, at pH values in excess of 8, the degree of extraction of boron falls sharply, especially in the case of extractants (IV) and (V). The organic solvents are re-extracted with a solution of alkali.

A promising extractant, Yarrezin-B, which is an aminophenol-formaldehyde polymer, has been developed[67] for the extraction of boron. The extractant has undergone industrial tests.

Alkylcatechols and hydroxymethyl derivatives of alkylphenols have been proposed as extractants.[68] In the presence of added aromatic amines, these substances extract boron from neutral and weakly acid solutions. They are re-extracted with solutions of inorganic acids.

Studies directed towards the search for effective boron extractants are being continued. It is noteworthy that extraction is a promising method for the removal of boron from brines, having advantages such as ease of automation, high rate of the process, continuous operation, and high purity of the product obtained. However, the method also suffers from serious disadvantages, which limit its application: complexity of the equipment and partial solubility of the organic extractants in water, which leads to the loss of expensive reagents and create an ecological problem.

VI. Thermal methods for the elimination of boron-containing substances from waste waters

Thermal methods for the extraction of boron from industrial liquid waste are of definite interest in some cases. We shall consider below some of them.

The method based on evaporation ensures the complete utilisation of boron-containing compounds and the liquidation of boron-containing liquid waste. After evaporation, the cooled solutions are treated with seeding crystals, increasing thereby the degree of salting-out of boric acid. This technology has been developed for the etching and moulding of a foil, where the content of boric acid is 10 g litre^{-1}.

The waste waters from electroplating industry, containing fluoroborates, are also treated by evaporation. The improvement of this method compared with that described above consists of the fact that the waste waters are treated beforehand with an alkali metal hydroxide until the attainment of pH 8 and the precipitated metal hydroxides are separated. This prevents encrustation of the apparatus.

Evaporation is frequently used in the purification of boron-containing waste waters from atomic power stations.[69] Radioactive waste waters containing boric acid at a concentration less than 2.4% are treated with soda-lime until the attainment of pH 6.8–7.7. The

liquid waste is then concentrated by evaporation until a boric acid concentration of 25–54% is reached. The distillate is cooled and discarded into a water-containing area, while the concentrated liquid waste is directed to a settling tank where boric acid crystallises on cooling. In order to reduce the pH and intensify the crystallisation process, the still residue is treated with oxalic acid. The supernatant liquid is treated with a solution of potassium permanganate and is directed to the evaporation apparatus.

A procedure for the purification of waste waters containing boron compounds and organic substances has been proposed.[70] It consists of the fact that the water is heat-treated in the presence of steam in an amount permitting the conversion of a major proportion of the boron into H_3BO_3. The method makes it possible to regenerate heat and boric acid, but is highly energy consuming.

In the general case, thermal purification methods are energy consuming, while in combination with other methods they greatly complicate the technology.

VII. Other methods for the isolation of boron from aqueous solutions

A fairly considerable amount of attention has been devoted to the extraction of boron from aqueous systems by electrochemical methods and by reverse osmosis. These procedures are of interest for the preparation of highly pure boron-containing products and also when it is necessary to eliminate boron compounds thoroughly from aqueous systems.

Liquid membranes based on β-diols, placed between two semiconducting partitions, have been proposed[71] for the extraction of boric acid. The β-diols employed were 2-butyloctane-1,3-diol, 2-propylheptane-1,3-diol, and nonane-1,3-diol dissolved in heptane, benzene, chlorobenzene, and isopentyl alcohol. The degree of extraction of boric acid from solutions increases linearly from 45 to 87% with increase in the concentration of the diols in the liquid membrane from 10^{-3} to 10^{-1} M and the current density is 0.5–10 mA cm^{-2}. In all cases, the highest percentage extraction of borate ions through the membrane is observed when isopentyl alcohol is used as the solvent for the liquid membrane, while the smallest effect is obtained when benzene is employed. Studies[72] on the influence of the pH in the electrodialysis of boron-containing waters showed that the optimum pH for the process is in the range 9.1–9.6.

By varying the composition of the liquid membrane, it is possible to achieve fairly complete extraction and concentration of boric acid from aqueous salt solutions. Electrochemical purification is also carried out with the aid of ion-exchange diaphragms, consisting of films of an ion-exchange resin and a filler. The diaphragms have a low hydrodynamic permeabilty and in water their intrinsic electrical conductivity is also low.[9] Apart from concentrating boron-containing solutions, electrolysers with ion-exchange membranes can find applications in the selective electrochemical decomposition of a boron-containing raw material.

A technology has been proposed[73,74] for the purification of boron-containing waste waters formed in the nickel-plating process. It involves reverse osmosis. In the first stage at pH 6, nickel is separated, after which the second purification stage is carried out. The boric acid concentrate obtained in the second stage is utilised.

Heterocyclic polymeric materials, including fluorinated and modified polyamides, are used[75] as the membrane material in the elimination of boron from waste waters by reverse osmosis. Thus, when a polypiperazineamide membrane is used at a pH of the medium of 8.4, the degree of extraction of boron is 83%, while at pH 11 the efficiency increases to 95%.

A cascade of reverse osmosis apparatus has been used for the extraction of boric acid from the waste waters generated by atomic power stations.[76] The process is carried out at pH 5–6.5 and at the ambient temperature.

A membrane, obtained by depositing a cellulose acetate film on a polyamide film, has been developed.[77,78] The active surface of the polyamide film was subjected to preliminary treatment with compounds selected from the $CaMoO_4$, $CoWO_4$, $PbWO_4$, $CaWO_4$, etc. group. The selectivity of this membrane is higher by 11.3% and its productivity is higher by 14.5% than those of the usual double membrane.

The employment of the electrochemical method as well as the reverse osmosis method for the extraction of boron compounds from aqueous solutions requires further study and improvement of the design of the electrolysers and of the quality of the membranes.

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As can be seen from the data presented above, boron is extracted from aqueous systems by means of a series of methods. The choice of the method of purification depends significantly on the concentration of boric acid in the waste water.

The elimination of boron from water by coprecipitation with gel-like metal hydroxide deposits entails costs associated with the regeneration of the deposits. This method has not been applied widely in technology.

The extraction of boron by organic compounds is a fairly effective and selective method when the boric acid content is in excess of 3 g $litre^{-1}$ and has a number of advantages. However, the method suffers at the same time from serious disadvantages, which limit its application: complexity of the equipment and partial solubility of the organic extracts in water, which creates an ecological problem.

The procedure based on evaporation is energy consuming and when combined with other methods appreciably complicates the technology.

The methods for the extraction of boron with the aid of ion-exchange materials of different kinds have been developed mainly for aqueous solutions with a relatively low (up to 2–3 g $litre^{-1}$) boric acid content. The low exchange capacities and the lack of selectivity of the majority of resins in relation to boron compounds make their practical use fairly complicated.

The commonest method for the extraction of boric acids from waste waters is the reagent method involving the precipitation of boron by lime water in the form of the sparingly soluble calcium borate. The method has proved itself in aqueous systems with concentrations of 1.3–1.5% in terms of B_2O_3.

It is essential to note that the usefulness of a method for the extraction of boron from waste waters must be considered for each specific case.

References

1. G Kh Effendiev *Khimiya Boratov* (The Chemistry of Borates), Zinatne, Riga, 1978, 148 pp.
2. L D Kurshakova *Fiziko-khimicheskie Usloviya Obrazovaniya Borosilikatnykh Mestorozhdenii* (Physicochemical Conditions Governing the Formation of Borosilicate Deposits), Nauka, Moscow, 1976, 274 pp.
3. E K Kaverzin, Yu S Plyshevskii, A Ya Futoryanskii *IV Oblastnaya Nauchno-Tekhnicheskaya Konferentsiya po Khimii i Khimicheskoi Tekhnologii. Perm* (The IVth Regional Scientific-Technical Conference on Chemistry and Chemical Engineering. Perm), Perm, 1973, Part 1, p. 47
4. E K Kaverzin, Candidate's Thesis in Technical Sciences, Mendeleev Moscow Institute of Chemical Engineering, Moscow, 1988, 16 pp.
5. G K Gode *Sintezy Boratov* (The Syntheses of Borates), Zinatne, Riga, 1971, Part 1, 58 pp.
6. K V Tkachev, Yu S Plyshevskii *Tekhnologiya Neorganicheskikh Soedinenii Bora* (Technology of Inorganic Boron Compounds), Khimiya, Leningrad 1983, 208 pp.
7. A I Rodionov, O M Voitova, N Ya Romanov, et al. *Elimination of the Products of the Combustion of Boron-containing Hydrocarbons from Waste Waters*, Moscow, 1990, 21 pp., Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 12.12.90, No. 6204
8. E P Ozhigov, V S Lozinskaya *Sbornik Referatov Dokladov IX Mendeleevskogo S'ezda* (Collected Abstracts of the IXth Mendeleev Congress), Khimiya, Moscow, 1965, p. 61
9. Yu S Plyshevskii *Tezisy Dokladov Nauchno-Tekhnicheskoi Konferentsii. Dal'negorsk* (Abstracts of Reports at a Scientific-Technical Conference. Dal'negorsk), Dal'negorsk, 1976, p. 116
10. M E Pozin *Tekhnologiya Mineral'nykh Solei* (Technology of Inorganic Salts), Khimiya, Leningrad, 1974, Part 1, 791 pp.
11. A I Goryachkin, E B Kislykh *Khim. Prom.*, 1949, **82** 1236
12. E M Shvarts, A F Ievin'sh *Sbornik Referatov Dokladov IX Mendeleevskogo S'ezda* (Collected Abstracts of the IXth Mendeleev Congress), Khimiya, Moscow, 1965, No. 7, p. 111
13. V V Vol'kin, A I Nenashev, A G Kozintsev *Zh. Prikl. Khim.*, 1983, (4) 767
14. A M Khodzhamamedov, K I Ismailov *Izv. Akad. Nauk Tadzh. SSR. Ser. Fiz.-Tekh. Khim. i Geol. Nauk.*, 1980, (3) 77
15. R E Zhaimina, B S Balapanova, G P Kosenko *Khimiya Kislorodnykh Soedinenii Bora. V Vsesoyuznoe Soveshchanie. Tesizy Dokladov. Riga* (The Chemistry of Oxygen Compounds of Boron. The Vth All-Union Conference. Abstracts of Reports. Riga), Riga, 1981, p. 55
16. A N Khodzhamamedov *Khimiya i Tekhnologiya Neorganicheskikh Sorbentov. Tezisy Dokladov. Ashkhabad* (The Chemistry and Technology of Inorganic Sorbents. Abstracts of Reports. Ashkhabad), Ashkhabad, 1982, p. 106
17. A N Nuriev, I K Ataev *Deposition of Boron from the Darydagsk Thermal Waters in the Form of Sparingly Soluble Compounds*, Moscow, 1982, p. 18, Deposited at the All-Union Institute of Scientific and Technical Information, 24.02.82, No. 1272-82
18. USSR P. 1 033 182; *Byull. Izobret.*, 1981, (10) 12
19. R E Zhaimina, S V Imanalieva, S M Ureketeva *Izv. Akad. Nauk Kazakh. SSR. Ser. Khim.*, 1979, (1) 6
20. L I Boltenkova *Khimiya i Tekhnologiya Neorganicheskikh Sorbentov. Tezisy Dokladov. Ashkhabad* (The Chemistry and Technology of Inorganic Sorbents. Abstracts of Reports. Ashkhabad), Ashkhabad, 1982, p. 104
21. USSR P. 946 647; *Byull. Izobret.*, 1980, (8) 11
22. USSR P. 449 012; *Byull. Izobret.*, 1985, (12) 7
23. A A Pospelov *Vsesoyuznaya Konferentsiya po Ionnomu Obmenu. Tezisy Dokladov Moskva* (All-Union Conference on Ion Exchange. Abstracts of Reports. Moscow), Moscow, 1979, p. 85
24. A U Rosombetova *II Vsesoyuznaya Konferentsiya po Kompleksnomu Ispol'zovaniyu Rud i Kontsentratov. Tezisy Dokladov. Moskva* (The IInd All-Union Conference on the Combined Utilisation of Ores and Concentrates. Abstracts of Reports. Moscow), Moscow, 1983, p. 98
25. A M Khodzhakuliev *Khimiya i Tekhnologiya Neorganicheskikh Sorbentov. Tezisy Dokladov. Ashkhabad* (The Chemistry and Technology of Inorganic Sorbents. Abstracts of Reports. Ashkhabad), Ashkhabad, 1982, p. 107
26. V Nikolaev *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1975, (1) 29
27. M A Rodionova, A I Mun, Z N Lukonina *Izv. Akad. Nauk Kazakh. SSR. Ser. Khim.*, 1976, (6) 7
28. R E Zhaimina, A I Mun, B S Baklamova *Izv. Akad. Nauk Kazakh. SSR. Ser. Khim.*, 1974, (6) 3
29. R E Zhaimina, B S Baklanova, A I Mun *Khimiya i Tekhnologiya Udobrenii Alyumosilikatov i Neorganicheskikh Sorbentov* (The Chemistry and Technology of Fertilisers, Aluminosilicates and Inorganic Sorbents), Nauka, Alma-Ata, 1975, No. 89
30. R E Zhaimina, B S Baklanova, N A Karatanov *Khimiya i Tekhnologiya Udobrenii Alyumosilikatov i Neorganicheskikh Sorbentov* (The Chemistry and Technology of Fertilisers, Aluminosilicates and Inorganic Sorbents), Nauka, Alma-Ata, 1975, No. 93
31. R E Zhaimina, B S Baklanova, N A Karatanov *Kondensirovannye Fosfaty, Soli i Alyumosilikaty iz Mineral'nogo Syr'ya Kazakhstana* (Condensed Phosphates, Salts, and Aluminosilicates from the Mineral Raw Materials of Kazakhstan), Nauka, Alma-Ata, 1978, p. 63
32. A I Mun, M A Rodionova, Z N Lukonina *Khimiya i Tekhnologiya Udobrenii, Solei i Alyumosilikatov* (The Chemistry and Technology of Fertilisers, Salts, and Aluminosilicates), Nauka, Alma-Ata, 1974, p. 66
33. R P Korosteneva, I K Gorbunov, A S Kishin *Vodosnabzhenie i Kanalizatsiya*, 1984, 151
34. US P. 3 952 085; *Chem. Abs.*, 1975, **85** 67352
35. Japanese P. 3 953 572; *Chem. Abs.*, 1981, **84** 3125
36. G K Pogenkohf *Environ. Sci. Technol.*, 1982, **16**(9) 609
37. USSR P. 827 388; *Byull. Izobret.*, 1979, (10) 27
38. N B Galitskaya, A K Ponomareva, A I Zernov *Ionoobmennye Materialy* (Ion-Exchange Materials), 1983, p. 84
39. R E Zhaimina, S V Imanalieva *Tr. Inst. Khim. Nauk Akad. Nauk Kazakh. SSR*, 1973, (36) 76
40. R E Zhaimina, A I Mun *Izv. Akad. Nauk Kazakh. SSR. Ser. Khim.*, 1972, (1) 72
41. N I Obertanov *Vestn. Khim.-Tekhnol. Inst.*, 1972, (8) 119
42. R S Abdulaeva, I K Ismailova *Issledovaniya v Oblasti Neorganicheskoi i Fizicheskoi Khimii* (Studies in Inorganic and Physical Chemistry) (Edited by K S Khabuleeva), Baku, 1977, p. 180
43. USSR P. 539 833; *Byull. Izobret.*, 1974, (8) 13

44. A N Nuriev, I K Abaev, I N Akhmetov *Azerb. Khim. Zh.*, 1982, (2) 112
45. USSR P. 948414; *Byull. Izobret.*, 1980, (9) 14
46. I V Samberskii, A G Shakhin, I K Leonov *Teoriya i Praktika Sorbtsionnykh Protsessov*, 1981, (14) 90
47. N B Galitskaya, I G Samsonov, I K Shilin *Ionoobmennye Materialy* (Ion-Exchange Materials), 1983, p. 84
48. I G Klimov, I V Alekseev, B V Tomskii *Tr. Inst. NIITEKhIM*, 1983, 45
49. E A Materova *Vestn. Leningr. Univ., Fiz.-Khim.*, 1965, No. 22(4) 365
50. L I Boltenkova, A M Khodzhamamedov, V G Morozova, et al. *Ionoobmennye Materialy v Narodnom Khozyaistve* (Ion-Exchange Materials in the National Economy), Nauka, Moscow, 1977, p. 68
51. A M Khodzhamamedov, L I Boltenkova *Sostoyanie Razrabotok po Izvlecheniyu Ioda, Broma i Mikroelementov iz Promyshlennykh Vod. Tezisy Dokladov. Saki* (The State of the Developments in the Extraction of Iodine, Bromine, and Microelements from Industrial Waters. Abstracts of Reports. Saki), Saki, 1982, p. 33
52. L I Boltenkova, A M Khodzhamamedov, V G Morozova *Vsesoyuznaya Konferentsiya po Ionnomu Obmenu. Tezisy Dokladov, Moskva* (All-Union Conference on Ion Exchange. Abstracts of Reports. Moscow), Moscow, 1979, p. 167
53. E I Azarova *Izv. Akad. Nauk Tadzh. SSR. Ser. Fiz.-Tekh., Khim. i Geol. Nauk*, 1980, (1) 68
54. R E Zhaimina, A I Mun, B S Baklanova *Izv. Akad. Nauk Kazakh. SSR. Ser. Khim.*, 1979, (1) 6
55. M A Rodionova, A I Mun, Z N Lukonina *Izv. Akad. Nauk Kazakh. SSR. Ser. Khim.*, 1971, (4) 16
56. L I Boltenkova, A M Khodzhamamedov, V G Morozova *Khimiya i Tekhnologiya Neorganicheskikh Sorbentov. Tezisy Dokladov. Ashkhabad* (The Chemistry and Technology of Inorganic Sorbents. Abstracts of Reports. Akhkhabad), Ashkhabad, 1982, p. 104
57. G K Gode *Khimiya Boratov* (The Chemistry of Borates), Izd. Akad. Nauk Latv. SSR, Riga, 1953, p. 105
58. USSR P. 158266; *Byull. Izobret.*, 1985, (11) 9
59. A L Grekovich *Kislorodnye Soedineniya Bora. Tezisy Dokladov. Riga* (Oxygen Compounds of Boron. Abstracts of Reports. Riga), Izd. Latv. Gos. Univ., Riga, 1967, p. 107
60. USSR P. 785321; *Byull. Izobret.*, 1986, (10) 10
61. Japanese Appl. 55-96681; *Chem. Abs.*, 1979, (83) 39361
62. Japanese Appl. 55-94680; *Chem. Abs.*, 1979, (83) 39361
63. Japanese Appl. 55-94682; *Chem. Abs.*, 1979, (83) 33362
64. USSR P. 401390; *Byull. Izobret.*, 1983, (12) 21
65. Bulgarian P. 24282; *Byull. Izobret.*, 1977, (5) 9
66. R T Ignat, I A Kalve, E M Shvarts *Khimiya Kislorodnykh Soedinenii Bora. V Vsesoyuznoe Soveshchanie. Tezisy Dokladov. Riga* (The Chemistry of Oxygen Compounds of Boron. The Vth All-Union Conference. Abstracts of Reports. Riga), Riga, 1981, p. 16
67. A L Grebovich *Vestn. Leningr. Univ., Fiz. Khim.*, 1969, No. 10(3) 298
68. V L Anikin, B A Petrov, G D Kharlamkvrich *Khimiya Kislorodnykh Soedinenii Bora. V Vsesoyuznoe Soveshchanie. Tezisy Dokladov. Riga* (The Chemistry of Oxygen Compounds of Boron. The Vth All-Union Conference. Abstracts of Reports. Riga), Riga, 1981, p. 16
69. BRD Appl. 3110491; *Chem. Abs.*, 1981, (7) 358
70. Japanese Appl. 55-85420; *Chem. Abs.*, 1980, (85) 67142
71. V N Golubev, L M Mel'nikova, E M Shvarts *Khimiya Kislorodnykh Soedinenii Bora. V Vsesoyuznoe Soveshchanie. Tezisy Dokladov. Riga* (The Chemistry of Oxygen Compounds of Boron. The Vth All-Union Conference. Abstracts of Reports. Riga), Riga, 1981, p. 80
72. A K Korolev, A A Levchenko *Khimiya Kislorodnykh Soedinenii Bora. V Vsesoyuznoe Soveshchanie. Tezisy Dokladov. Riga* (The Chemistry of Oxygen Compounds of Boron. The Vth All-Union Conference. Abstracts of Reports. Riga), Riga, 1981, p. 85
73. Japanese P. 56-12195; *Chem. Abs.*, 1981, (84) 67142
74. Japanese Appl. 57-162692; *Chem. Abs.*, 1982, (83) 72131
75. French Appl. 2554732; *Chem. Abs.*, 1981, (12) 2345
76. DDR P. 153015; *Chem. Abs.*, 1980, (10) 1021
77. A L Trenovich, I K Lobanov *Zh. Prikl. Khim.*, 1970, **15**(1) 38
78. A M Lazareva, I K Mishin, K V Sheklin *Zh. Prikl. Khim.*, 1968, **41**(11) 1106