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Reagent neutralization of chromium-containing inhibitor solution

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Abstract

The problem of neutralising liquid solutions containing hexavalent chromium compounds is considered. The advantages, disadvantages and features of the application of basic methods for neutralising chromium-containing waste, non-traditional approaches and combined technologies are analysed. A readily feasible reagent method is presented for purifying concentrated and dilute solutions from chromium by treatment in two stages: reduction of hexavalent to trivalent chromium using ferrous sulphate or sodium sulphite as reducing reagents, and precipitation of chromium hydroxide. An installation is described in which electrolytes, rinsing and waste water from galvanic production were neutralised. A practical approach to the problem of neutralising the inhibitor solution is proposed, which is similar to the methods used for processing chromium-containing waste from galvanic production. A technological process has been developed for the reagent treatment of an inhibitor with a high concentration of chromates in solution (up to 40 g/L) in one stage by the direct precipitation of poorly soluble chromates. Barium chloride was used as the precipitant. To implement the technology, a schematic diagram of the installation was developed, and appropriate equipment was selected. As a result of processing the inhibitor, waste water, heavy precipitate of barium chromates are formed, which can be used in the future as a raw material, and sludge, which is a non-recyclable waste. Experimental processing of the inhibitor solution shows that the proposed method is effective, economically feasible, readily implementable under industrial conditions, it allows for high purification degree with low consumption of reagents, and reduces the amount of precipitates formed, which confirms the practical significance of the results obtained.

Keywords: corrosion inhibitor, chromium, reagent treatment, barium chloride, neutralisation, precipitation

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INTRODUCTION

Corrosion inhibitors (below referred to as inhibitors) containing chromium are widely used in many branches of industry, specifically in metallurgy, automobile production, oil refining, to increase the operational life of metal parts, decrease expenses for repair and service, and enhance the reliability of equipment. A working medium in shielding tanks at some atomic-powered submarines is a chromium-containing inhibitor solution, which provides cooling of the reactor and other submarine systems. The volume of a shielding tank filled with the inhibitor may range from

several ten to one hundred and fifty tons [1]. After reaching the end of a useful life, inhibitor solutions from these tanks are to be neutralised in agreement with the requirements of environmental safety. Neutralisation may involve inhibitor solution processing for repeated use or for obtaining other chemicals. If an inhibitor solution cannot be processed, it is to be disposed in accordance with the requirements of environmental safety using the methods that do not cause environmental hazard.

Neutralisation of the large volumes of spent solutions is associated with solving several problems. First of all, it is safety, because inhibitors from shielding tanks are based on potassium chromate and belong to the first substance hazard category, which brings about danger for environment and for humans [2]. Neutralisation process involves technical and technological complications related to the development of special equipment and fittings.

There are several approaches to neutralise the solutions containing toxic compounds of hexavalent chromium, in particular reagent purification, electric and galvanic coagulation, membrane technologies, and adsorption purification. Innovative approaches, for example those involving nanomaterials, photocatalytic processes, etc., also appear to be promising for neutralisation of chromium-containing solutions.

The goal of the present work is to analyse the modern methods for treating the liquid chromium-containing wastes, to investigate the possibility to neutralise the chromium-containing inhibitor solution using the reagent method in a single stage, to determine the optimal parameters of additional purification for obtaining neutralised solution, and to develop the basic concept of an installation to implement the technological process.

ANALYSIS OF THE METHODS FOR CHROMIUM-CONTAINING WASTE TREATMENT

The approach to the neutralisation of chromium-containing inhibitor solutions can be similar in its principles to the methods used to neutralise the chromium-containing wastes from galvanic works, such as the rinse waters from specific technological operations or spent electrolytes from chromium plating.

Reagent treatment can be implemented using two methods. One of them implies the direct precipitation of poorly soluble chromates in a single stage. In this case, chromium-containing solutions are treated with the reagents that can bind chromium, transform it into the insoluble form, and form heavy precipitates. The reagents used for this purpose include solid barium carbonate, barium hydroxide, or a solution of barium chloride. The product formed in this reaction is crystalline barium chromate ($BaCrO_4$), it is readily precipitated in the neutral or weakly acidic medium, and is removed by filtering off [3].

The second widely used method includes two stages. In this case, chromium-containing solutions are initially treated with the reagents that reduce hexavalent chromium into trivalent one. Then, after reduction, chromium is precipitated in the form of hydroxide. Examples of the reagents of this kind are sodium salts of sulphuric acid, ferrous sulphate, etc. The choice of a reagent depends on specific conditions and requirements.

A method for the purification of waste waters from electrolytic chromium production and chromium-plating containing chromium within the concentration range of 2 to 90 g/L (recalculated to CrO_3) is proposed in [4]. As a result of waste water treatment with barium hydroxide, trivalent and hexavalent chromium is precipitated, and after precipitate removal, a solution is formed that can be readily neutralised, for example, by sulphuric acid. The low value of solubility product (SP) for $BaSO_4$ allows one to purify the solution from barium and return the purified waste waters for technological purposes. However, using this method, it is necessary to keep in mind the toxicity of barium and its compounds, so all safety precautions are to be followed when handling them. Another example of single-stage treatment is waste water purification by treating them with barium hydroxide in the presence of calcium hydroxide, taken in the amount of 1.8–9.0 g per 1 g of hexavalent chromium present in the waste water. Purification degree is 95.67–96.27 % [5].

Reagent treatment with a 10 % aqueous solution of sodium sulphite or disulphite in acid medium at pH 1.5–2 was used to neutralise the non-standard inhibitor from shielding tanks was described in [1]. After reduction of hexavalent chromium, the solution was pumped along pipelines and treated together with the acid-alkaline waste waters from the galvanic works to precipitate insoluble chromium hydroxide in alkaline medium at pH 8–9.

The authors of [6] used a combined scheme to treat chromium-containing waste waters: reagent precipitation of chromium in the form of hydrox-

ide, using ferrous sulphate ($FeSO_4$) as the main reagent, followed by floatation-based isolation of the precipitate, which allows an increase in the extent of chromium recovery. As a result, $Fe(OH)_3$ is also removed by floatation from the solution together with $Cr(OH)_3$.

A two-stage method of the complete purification of waste waters from chromium compounds is proposed in [7]. At the first stage, Cr(VI) is reduced by sodium sulphite, and then purified by modified shungite. With this combination of the processes, the authors have succeeded in achieving a complete (100 %) removal of chromium compounds from the solution.

Sorption-based method was proposed to purify solutions after hexavalent chromium is transformed into trivalent one [8]. For this purpose, a filtering charge composed of the modified aluminosilicate adsorbent is used, which is manufactured from kaolinite with a modifying additive containing magnesium and calcium cations. While chromium-containing solution is filtered through the adsorbent layer, chromium ions react with OH^- group in the alkaline medium to form hydroxides. In turn, chromium hydroxides form negatively charged micelles, which are attracted to the granules of activated aluminosilicate adsorbent, thus forming gel-like colloid structure inside the filtering charge. For the additional purification of chromium-containing waste waters, the sorption method is proposed, involving the use of modified sorbent as pastes obtained on the basis of bentonite clay and wood chips, introduced as a modifier [9].

The possibility to reduce Cr(VI) into Cr(III) at not very high chromium concentrations in the waste waters using non-traditional reagents based on the chips of deciduous and coniferous wood has been demonstrated in [10]. The powdered modified active coal samples were used as sorbents to purify chromium-containing waste waters as described in [11].

Efficient purification methods also include electric coagulation, the advantages of this method are described in [12]. This method allows efficient purification of chromium-containing waste waters with the complex multicomponent composition of pollutants. The highest purification degree is achieved using the combined method based on preliminary electric coagulation, followed by electric floatation. To implement this method, the authors used electric floatation coagulator device, equipped with the chamber for electric floatation, in addition to the electric coagulation chamber.

To reduce energy consumption for electric coagulation, the authors of [13] studied a technological process of the joint treatment of oil emulsion chromium-containing waste water applying the asymmetric alternating current. A decrease in energy consumption by a factor of 2.5 was demonstrated, while the purification degree remained high.

To purify chromium-containing waste waters formed in galvanic works, an experimental installation was presented in [14], and the galvanic coagulation method was tested, demonstrating the possibility of efficient purification. Experiments aimed at determining the rational modes of galvanic coagulation purification of chromium-containing wastes have shown that Cr(VI) concentration in the acid medium decreases to 0.01 mg/L [15].

In contrast to galvanic or electric coagulation, the authors of [16, 17] describe neutralisation of chromium-containing waste waters (with chromium anhydride concentration 1–400 g/L) without using galvanic pairs or external electric current. The proposed method is based on the use of steel cuttings as a reducing agent for hexavalent chromium. Its advantage is the single-stage process with simultaneous removal of chromium compounds form solution and the formation of ferrochromium precipitate, which is a valuable raw material for metallurgic industry.

Possible alternatives to the traditional methods of chromium removal from industrial waste waters are nanofiltration and reverse osmosis. It is demonstrated in [18] that the degree of purification from hexavalent chromium using a nanofiltration membrane depends on the initial chromium concentration in solution, pH, and the presence of other pollutants, and can reach 99.7 %. With the reverse-osmotic membrane, the purification degree varies from 85 to 99.9 %.

Each of the technologies used to treat chromium-containing solutions has its own shortcomings, limitations for practical implementation. Reagent methods are relatively simple, and they can be used to treat large volumes of solutions. However, their disadvantages include the formation of toxic precipitates, high expenses for chemical reagents, the necessity to prepare them and to provide services for the complex reagent facilities. The sorption method is distinguished by environmental safety, high efficiency, and does not require complicated equipment. Its application can be limited due to the high cost of sorb-

ents, the necessity to replace them on a regular basis, and later on to provide their regeneration or disposal. In addition, the sorption method is not always suitable for the purification of solutions with high chromium concentrations. The electric coagulation method provides the possibility to treat highly concentrated chromium-containing solutions, which is accompanied by a decrease in the amount of precipitates, and reagent consumption decreases substantially. However, the essential disadvantages of this method are the necessity of permanent control over process conditions and high energy consumption. Galvanic coagulation is distinguished by rather low energy consumption and operation expenses, but the application of this method requires the excessive amount of the reagent (iron turnings), the procedure of charge replacement is labour-intensive, and large amounts of difficult-to-dehydrate precipitates are formed. The ion exchange method exhibits high purification efficiency, but it requires substantial investment into the equipment, expenses for ionite regeneration and resin treatment, as well as additional processing of secondary eluate wastes. Reverse osmosis is considered to be efficient, but its application is related to the necessity to use expensive, not readily available membranes and airtight operationally complicated installations. Electric floatation is simple to maintain, but this method requires preliminary dilution of concentrated solutions, so it can be used successfully in combination with other purification methods.

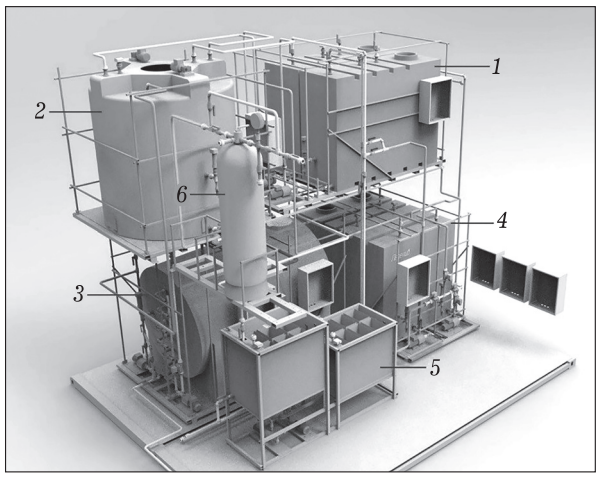

Fig. 1. Pilot installation for neutralisation of chromium-containing wastes: *1* – charging reservoir; *2* – neutralising reactor; *3* – clarifying reactor; *4* – filtrate reservoir; *5* – reducing reactor; *6* – filter for fine purification.

Comparing the above-considered methods for treating chromium-containing waste waters, we may state that the choice of an optimal scheme depends on specific conditions and requirements. Before using or introducing certain method, it is necessary to carry out additional studies, to assess its efficiency, safety, environmental impact, cost, process control complexity, and the possibility to treat large amounts of wastes.

Both in Russia and abroad, a widespread purification approach is a reagent method, in spite of its disadvantages, such as high reagent consumption and the formation of substantial amounts of sludge.

At the Institute of Chemistry, FEB RAS, the authors of the present work have carried out a number of studies to investigate the technological features of the treatment of concentrated and diluted chromium-containing solutions using reagent methods [19, 20]. The installation was developed (Fig. 1) and used to neutralise the spent electrolytes, washing and waste waters from the galvanic works [21].

For the two-stage treatment, independently of the kind of reagent used, chromium-containing wastes were accumulated in the charging reservoir (*1*), where solution averaging, parameter control, and correcting treatment were carried out. Reduction of hexavalent to trivalent chromium was conducted in neutralising reactor (*2*). After that, the reacted solution was poured into the clarifying reactor (*3*) to precipitate insoluble compounds formed during reagent treatment in the form of chromium hydroxide fractions. The clarified solution was supplied to the filtrate reservoir (*4*). In the case if additional purification is needed to reach the maximum permissible concentration (MPC), the purified solution can be supplied to the two-step-type reducing reactor (*5*) with the active charge composed of preliminarily prepared metal cuttings or to the sorption filter for fine purification (*6*).

Investigation of the processes involved in the purification of chromium-containing solutions allowed us to optimise the technological purification scheme, upgrade the experimental installation, and conduct neutralisation of the chromium-containing inhibitor solution using this installation [22]. Total chromium content in the solution was 1720 mg/L. The single-run volume of solution per one treatment cycle is 2500 L. The flow diagram of the installation for the treatment of the inhibitor is shown in Fig. 2.

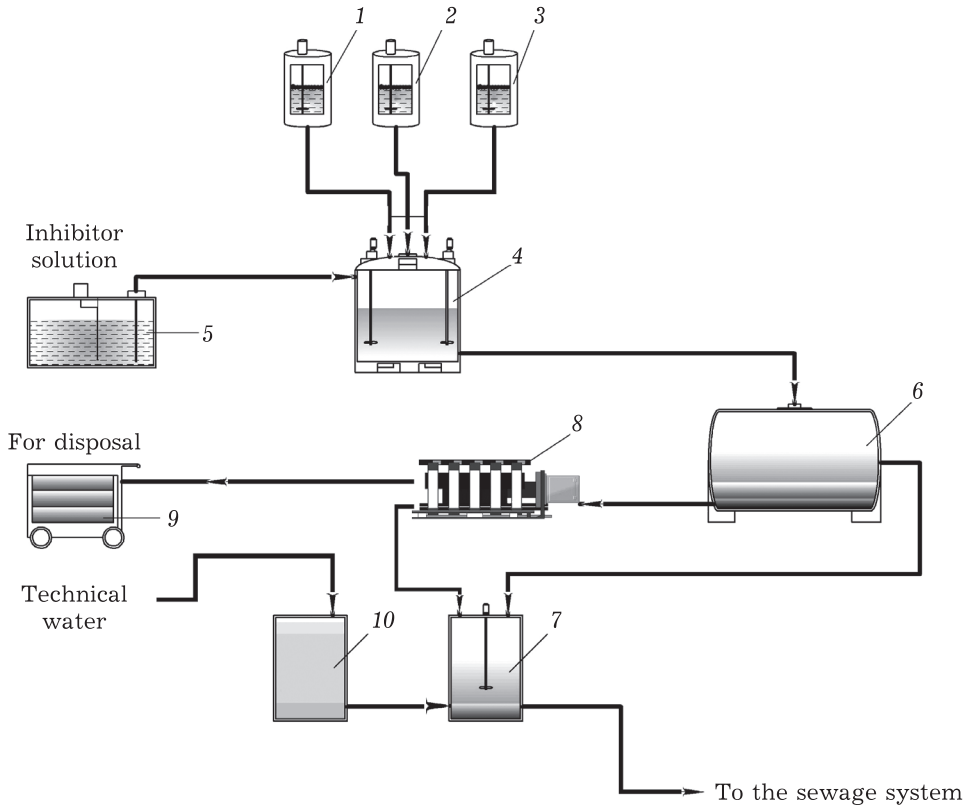

Fig. 2. Flow diagram of the pilot plant for two-stage treatment of the chromium-containing inhibitor solution: *1–3* – reagent reservoirs; *4* – neutralising reactor; *5* – reservoir for inhibitor storage; *6* – clarifying reactor; *7* – accumulating reactor; *8* – press filter; *9* – trolley; *10* – reservoir for technical water.

Reagent treatment was performed in two stages in the following sequence: Cr^{6+} reduction to Cr^{3+} → pH regulation → exposure for the reaction to be completed → precipitation of hydroxides ($Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3\downarrow$) → settling → separation of the solid residue from the filtrate. Reagent treatment was carried out with permanent control of pH, temperature, and reaction time. Sodium sulphite or ferrous sulphate was used as the main reagent. Reducing reagents were prepared in the form of a 10 % aqueous solution in the reagent reservoir (*1*), 20 % sulphur acid solution – in reservoir (*2*), 20 % alkaline solution – in reservoir (*3*) (see Fig. 2). The solutions were prepared by permanent mixing with built-in hydraulic mixers. Inhibitor solution was treated in the neutralising reactor (*4*). The inhibitor solution was supplied from the storage reservoir (*5*) in the necessary amounts using a pump. The reagents were supplied in the calculated amounts with dosing pumps. Precipitation proceeded in the neutralising reactor. The reacted solution was poured into the clarifying reactor (*6*), where it was settled until insoluble compounds (sludge) were formed. Then the clarified solution was transferred into the accumulating reactor (*7*). There, if necessary, the clarified solution was diluted with technical water from reservoir (*10*) to decrease salt content down to the MPC level, and then disposed into the sewage system. Sludge from the clarifying reactor was transferred to the press filter (*8*), then discharged from the press filter onto a trolley (*9*) and sent for subsequent processing.

The problem of sludge storage or utilisation presents severe difficulties at enterprises, so it is very important to choose reasonable reagents for neutralising chromium-containing solutions for the purpose of obtaining sludge suitable for subsequent processing, in particular by using them as secondary resources. To determine the possibility of deep processing of the sludge obtained by inhibitor neutralisation, the studies of precipitate samples were carried out. The results of X-ray diffraction analysis of sludge samples after annealing at a temperature of ~1000 °C revealed

the presence of oxides that can be reduced in the aluminothermic reaction. Aluminothermic reduction of dehydrated sludge implied the formation of environmentally safe products suitable for further use.

Analysis of the results of pilot plant tests and the treatment of chromium-containing wastes, in particular the inhibitor, has shown that the reduction proceeds at a high rate, and a high purification degree is achieved if reagents are precisely dosed. A substantial disadvantage of reagent treatment in two stages is the formation of large amounts of sludge, especially after the use of ferrous sulphate as a reducing agent. In addition, the precipitate after treatment with ferrous sulphate becomes loose, silt-like, and more difficult to dehydrate.

DESCRIPTION OF THE PILOT PROCESS AND PLANT OPERATION

Technology

The practical evaluation of the technological process of inhibitor solution neutralisation using the reagent method in one stage was performed with real wastes having no restrictions with respect to radiation safety.

The inhibitor to be processed was an aqueous solution of potassium chromate (K_2CrO_4) in fresh water. The major pollutant elements of the solution are the anions of hexavalent chromium compounds (CrO_4^{2-}). The content of Cr(VI) in the solution was determined to be within the range of 17.5–18.0 g/L. The presence of radioactive elements in the solution was not detected, the concentrations of other pollutants were insignificant, solution pH was 9.3–9.5. The purified solution should meet the following MPC standard values: Cr(III) not more than 0.5, Cr(VI) not more than 0.05, Fe not more than 5 mg/L. These requirements are specified by the norms adopted by the Decree of the Government of the Russian Federation of May 22, 2020, No. 728 [23]. The maximum permissible concentration of Ba in waste waters has not been enacted.

Determination of Cr, Fe, Ba concentrations in the samples was carried out by atomic absorption using a Thermo Solaar M6 spectrophotometer (USA). To obtain data quickly at the plant, the content of hexavalent chromium was assessed using a portable multiparameter analyser – HI 8320 colorimeter (HANNA Instruments, USA).

It is important to stress that when choosing inhibitor utilisation method, the inhibitor volume and concentration were also taken into account in addition to the environmental safety requirements. The main processing technology was accepted to be a reagent procedure based on the transformation of chromate ions into poorly soluble compounds (barium chromate). The main operations of the technological process are presented in Fig. 3.

To provide a correct calculation of the necessary amounts of reagents for the treatment of chromium-containing inhibitor, preliminary laboratory tests were carried out. This allowed us to reduce the excessive reagent consumption and save cost. The list of reagents, their amounts required to purify 1 m^3 of the inhibitor solution from hexavalent chromium in one stage are shown in Table 1. To assess the economic efficiency of the process, we also list the costs of reagents (see Table 1) necessary to perform the treatment process in two stages using sodium sulphite and ferrous sulphate as the main reducing reagents. The two-stage treatment was implemented by us previously using the installations (see Fig. 1 and 2).

Barium chloride was used as the main reagent for single-stage treatment. Inhibitor neutralisation was performed by Cr(VI) precipitation in the form of poorly soluble barium chromate $BaCrO_4$ ($SP = 1.2 \cdot 10^{-10}$) [24]. The precipitate was separated by settling and filtration. Then additional purification of the supernatant liquid from the residual amounts of chromium and from barium excess was carried out.

Barium chloride was prepared in the form of a 20 % aqueous solution, dosing was made with a slight excess (3–10) %, so that the dose was about 5 g per 1 g of Cr(VI) for the technical-grade reagent. Theoretical dosing of pure barium chloride for precipitation was 4 g per 1 g of Cr(VI), for barium chloride dihydrate – 4.7 g per 1 g Cr(VI).

The main reaction proceeding during precipitation is:

$$K_2CrO_4 + BaCl_2 \rightarrow BaCrO_4\downarrow + 2KCl \quad (1)$$

Barium chloride dosing for hexavalent chromium precipitation was performed using the instrumental method (based on pH changes). Specific features in pH changes during the main reaction (precipitation) were discovered: a smooth gradual increase in pH by 0.2–0.3 was observed with the addition of barium chloride solution to the inhibitor solution, and near the equivalence point we detected a jump-like increase in pH to

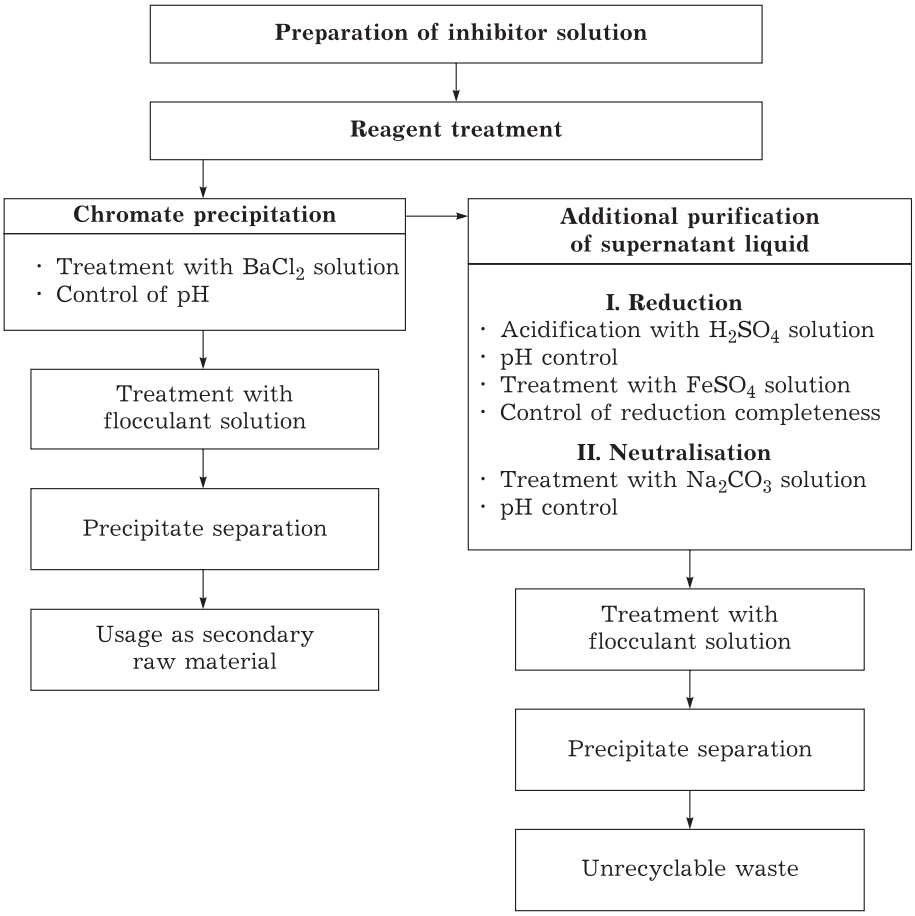

Fig. 3. Technological process of one-stage treatment of the inhibitor.

10.5–11.0, followed by a sharp drop to a level of <9. The yellow colouring of the solution was observed to disappear in this process, which confirmed the absence of hexavalent chromium. This sharp pH change was accepted as the equivalence point. The effect was detected and applied in implementing this technology to determine and control the necessary amount of barium chloride.

After reaction completion, the precipitate in the form of suspension was separated by settling and filtering. Settling time depended on the volume of the inhibitor under treatment, tempera-

TABLE 1

Reagents for treating 1 m^3 of the inhibitor using one- and two-stage methods

Reagent	Treatment in one stage using precipitation method	Treatment in two stages using reductive method		Cost* per 1 kg, RUB
Barium chloride dihydrate, Technical grade, kg	85–95	–	–	174
Sodium sulphite, technical grade, kg	0.1–0.5	65–75	–	150
Ferrous sulphate heptahydrate, technical grade, kg	0.03–0.1	–	290–330	69
Sodium carbonate, technical grade, kg	2–4	–	–	73
Sulphuric acid, technical grade, kg	0.8–1.0	85–90	–	54
Sodium hydroxide, technical grade, kg	–	45–50	55–60	90
Flocculant Praestol 650, kg:				
for precipitation	0.01–0.02	0.01–0.02	0.01–0.02	500
for additional purification	0.001–0.002	–	–	500
Total cost of treatment, thousand RUB/m^3	15.0–16.9	18.4–20.6	25.0–28.2	

Note. Dash – reagent was not used in a specific process.

* Approximate cost of reagents in 2024 for the Far Eastern Federal District.

ture, the use of a flocculant, and the design of a precipitating reactor. Before filtering, it is recommended to treat the mixture with a 0.1 % solution of commercial cationic flocculant Praestol 650 or its analogue. The flocculant was added in the dose of ~10 mL per 1 L of the working solution, and the mixture was stirred mechanically for 5 min at a low rotation frequency (80–200 r.p.m.).

The supernatant liquid was additionally purified from the residual amounts of Cr(VI) and from excessive barium. The residual content of Cr(VI) dissolved in the supernatant liquid was not more than 1 mg/L.

Additional purification was performed in two stages (reduction and neutralisation). Initially, the supernatant liquid was acidified with sulphuric acid to pH < 3. This process involved the transition of Cr(VI) from the captured barium chromate particles into the solution. After that, the acidified solution was treated with a reducing agent. To remove small amounts of hexavalent chromium, it is an efficient way to use ferrous sulphate in the dose of 30–50 g per 1 m^3 of the solution under treatment. The residual amount of Cr(VI) was reduced to Cr(III), Fe(II) was oxidised to Fe(III), and excessive barium was bound in the form of insoluble $BaSO_4$ ($SP = 1.1 \cdot 10^{-10}$) [24].

Additional purification of the supernatant liquid was carried out according to the following reactions:

$$BaCrO_4 + H_2SO_4 \rightarrow BaSO_4 + H_2CrO_4 \quad (2)$$

$$2H_2CrO_4 \rightarrow H_2Cr_2O_7 + H_2O \quad (3)$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \quad (4)$$

The completeness of Cr(VI) reduction was controlled visually by sampling and carrying out the reaction with diphenyl carbazide in the presence of sulphuric acid. Raspberry-red solution colouring provided evidence of the presence of a substantial residual amount of hexavalent chromium, rose colouring was evidence of its small amount. If the degree of solution purification from Cr(VI) turned out to be insufficient, additional calculated dose of ferrous sulphate was added.

After reduction, we carried out neutralisation of the purified water using the solution of sodium carbonate to pH 8–9. The ions Fe^{3+} and Cr^{3+} were precipitated in this process in the form of hydroxides:

$$2Fe^{3+} + 3CO_3^{2-} + 3H_2O \rightarrow 2Fe(OH)_3\downarrow + 3CO_2\uparrow \quad (5)$$

$$2Cr^{3+} + 3CO_3^{2-} + 3H_2O \rightarrow 2Cr(OH)_3\downarrow + 3CO_2\uparrow \quad (6)$$

The excess of Fe^{2+} and Ba^{2+} ions was removed in the form of practically insoluble carbonates:

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3\downarrow \quad (7)$$

$$Ba^{2+} + CO_3^{2-} \rightarrow BaCO_3\downarrow \quad (8)$$

For $BaCO_3$, $SP = 5.1 \cdot 10^{-9}$ [24]. The joint presence of insoluble barium salts and the hydroxides of iron and chromium promoted their joint coagulation. To improve precipitation, neutralised water was additionally treated with the solution of a cationic flocculant (Praestol 650) in the dose of 1–2 g/m^3. Analysis of the purified waste waters revealed the residual concentrations of Cr(VI) to be not more than 0.025, Cr(III) 0.1–0.3, Fe 0.1–0.3, Ba less than 2 mg/L, which did not exceed the adopted MPC levels.

Process instrumentation

To implement the technology of inhibitor processing, a process flow scheme of the pilot plant was developed, and proper equipment was chosen (Fig. 4). Taking into account the potential danger of the inhibitor and the reagents involved, which requires special precautions, the equipment was designed adhering to all necessary safety measures to prevent possible accidents, and special attention was paid to convenience for maintenance and service.

Preparation of the solution of barium chloride, which is the main reagent for chromate precipitation, presents difficulties because of its high toxicity. To provide safety and exclude manual operations, the bags with barium chloride powder are unpacked at the site of reagents preparation, where a bag tipping device (*1*) and bag splitter with a flexible conveyer (*2*) are provided. The solution is prepared using tap water in the dilution reservoir (*3*) at constant stirring with a mixer (M1) until the complete dissolution of $BaCl_2$ powder.

The maximal volume of inhibitor to be treated once in the installation described above is 500 L. The inhibitor from shielding tanks is poured into the precipitating reactor (*4*), which is intended for the removal of the main amount of chromium from solution and for accumulation of barium chromate precipitate. The reactor is a cylindrical vessel with a conical bottom made of semi-transparent plastics, 0.8 m^3 in volume. To provide mixing, the reactor is equipped with electromechanical stirrers (M2) and (M3), and the sensor of the pH meter.

The sensor which is used to determine pH possesses a high sensitivity to external conditions. It

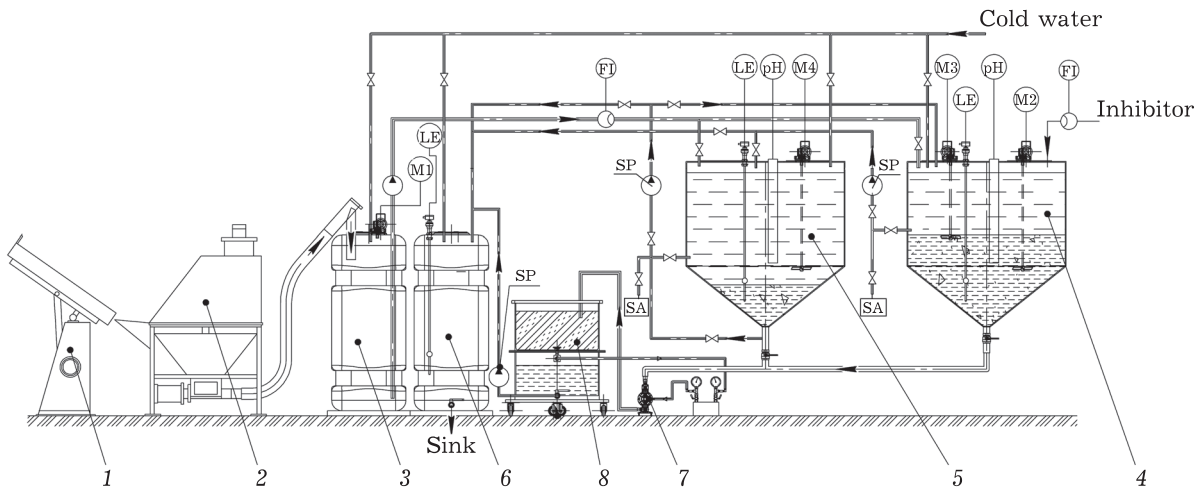

Fig. 4. Process flow scheme of the pilot plant for single-stage reagent treatment of the inhibitor: *1* – bag tipping device; *2* – bag splitter; *3* – dilution reservoir; *4* – precipitating reactor; *5* – neutralising reactor; *6* – accumulating reservoir; *7* – vacuum pump; *8* –Nutsche filter; M1–M4 – electric mechanical stirrers; pH – sensor of pH-meter; LE – level indicator; SP – supplying pump; SA – sampler; FI – flow meter.

is important to note that the working electric stirrers can have a negative effect on sensor functioning. For this reason, a protective housing intended for placing the cable with a pH sensor is provided in the reactor design. A glass tube of the electrode in the protective cover is mounted in a float (Fig. 5). This kind of sensor arrangement provides the possibility to carry out measurements independently of solution level in the reactor, allows taking measurements continuously without taking the sensor out of the protective housing, protects it from external action, such as vibrations, and provides insulation from possible mechanical damage.

Pipelines from the dilution reservoir (*3*) with barium chloride solution are laid to the precipitating reactor (*4*) (see Fig. 4). The supply of barium chloride solution from the dilution reservoir to precipitating reactor is regulated by the flow meter (FI) and is provided by a pump (SP) or through flow by gravity. The inhibitor is supplied by an external pump. The volume of supplied inhibitor solution was controlled using a flow meter, and the volume of solution in the reactor was measured with a level sensor (LE).

After completion of $BaCrO_4$ precipitation, it is separated by settling in reactor (*4*). Sampling is carried out manually through a sampler (SA).

For additional purification, the solution from the reactor (*4*) is supplied into the neutralising reactor (*5*) equipped with an electromechanical stirrer (M4) and pH-meter sensor. To decrease

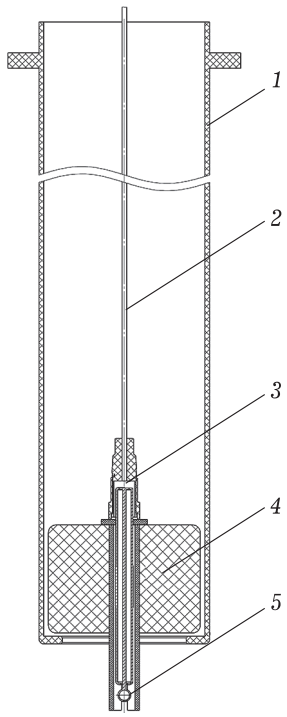

Fig. 5. Device for mounting pH-meter: *1* – protective housing; *2* – connector with a pH sensor; *3* – glass tube of the electrode; *4* – float; *5* – pH-sensitive membrane.

the contamination of liquid with the stirred precipitate, it is reasonable to discharge the liquid using a gravel-sand bed filter. Reactor (*5*) filling is regulated by a float level sensor (LE). Reagents, specifically the solutions of acid, reducing agent (ferrous sulphate), sodium carbonate and floccu-

lant, are supplied manually through a hatch in the reactor cap.

After additional purification of the solution in the neutralising reactor (*5*), purified water is poured off into an accumulating reservoir (*6*). Filling is regulated with a float level sensor (LE), purified water is disposed into the sewage system in a free flow of with a forcing pump.

To dehydrate the precipitate formed after main treatment in reactor (*4*) and after additional purification in reactor (*5*), water-flooded precipitate is pumped by a vacuum filter (*7*) onto Nutsche filters (*8*). While the precipitate is passing through the Nutsche filter, its volume decreases substantially, so does its humidity, so subsequent treatment and disposal are simplified.

Processing products

The experience obtained in the treatment of inhibitor with hexavalent chromium concentration 17.5–18.0 g/L has shown that the products and wastes formed after neutralisation of 1 m^3 of the inhibitor are: waste water in the amount of 1.5–2 m^3, barium chromate precipitate 100–130 kg in mass, sludge – up to 10 kg.

Waste water contains potassium chloride in the concentration of 20–30 g/L. It can be disposed into the sewage system of the enterprise or utilised as a potassium fertiliser. The content of Cr(VI), Ba and Fe in waste water does not exceed the maximum permissible norms [23].

Barium chromate precipitate with humidity 20–50 % relates to the first substance hazard category. The humid precipitate is the raw material that can be used as a pigment to manufacture corrosion-resistant coatings [25], as a corrector of the concentrations of solutions in galvanic chromium-plating baths (sulphate absorbing agent) [26], a component of pyrotechnic compounds (igniting and delaying compositions) [27, 28], and as a raw material for obtaining metal chromium and its compounds. To bring the material to the state of a commercial product, additional washing and drying will be required.

The sludge, 1 to 10 kg in mass, contains barium sulphate and carbonate, as well as admixtures of ferric hydroxides, chromium(III) hydroxides and ferrous carbonate. The mass of the formed sludge depends on the excess of barium chloride, which is used as the main reagent to precipitate chromates. The sludge is an unrecyclable waste of the III–IV substance hazard category.

CONCLUSION

Neutralisation of chromium-containing inhibitor solution at the pilot installation by reagent treatment using barium chloride as the main reagent allowed us to achieve positive results from the viewpoint of environmental safety, efficiency, resource saving, and waste minimisation. The pilot installation is simple in managing and maintaining, and it allows control over the process.

Barium chloride is supplied in the form of a 20 % aqueous solution to the chromium-containing inhibitor under controlled pH and temperature. As a result, heavy barium chromate precipitate is formed, which can be readily filtered off and removed from the solution. Ferrous sulphate is used in small amount if additional purification of the solution from residual chromium and barium excess is necessary.

One-stage reagent treatment of the chromium-containing inhibitor by the direct precipitation of chromates has advantages over the two-stage reagent treatment because it excludes the additional stage of hexavalent chromium reduction, thus decreasing the number of technological operations. The process gains in simplicity and rate. In addition, expenses for reagents and their preparation decrease substantially. Taking into account the amount of inhibitor solution treated under industrial conditions, which was 40 m^3, cost saving for reagents alone was 136–148 thousand roubles in comparison with the two-stage treatment with sodium sulphide, and 400–452 thousand roubles against ferrous sulphate. Furthermore, in the case of direct precipitation of chromium compounds, the amount of the formed precipitates requiring subsequent treatment, washing, dehydration, disposal or storage is substantially lower. This is one of the key advantages because a decrease in the amount of wastes reduces the environmental load.

Results of the studies can be used for developing the technologies and equipment for the purification of liquid chromium-containing wastes using the reagent method and combined treatment methods.

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