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Risk Management of Implementation of Reagentless Treatment of Acid Mine Water

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Abstract: The task of managing the risk of introducing reagentless treatment of acid mine water is considered. The task is solved, first of all, for natural technological complexes formed by coal and copper-zinc-pyrite mines transferred to "wet" preservation due to unprofitability. To solve the problem, a mobile technological complex operating in a flow-through mode is used. The solution of the problem is based on a system decomposition of the object, tasks and research criteria. The object of the analysis are large volumes of heterogeneous flows of mine water arriving for treatment. The set task is a multi-criteria one. Multi-agent modeling integrating several applications interacting by means of input and output data flows is used for the system design. Decomposition of the set task on the basis of a joint study of mine water properties and treatment technology on a laboratory bench, on which it is possible to reproduce the minimum required set of treatment operations and water conditioning is performed. The structure of the system integrating the concept of safety and the concept of extraction of high value products from mine water is offered. Results of X-ray phase analysis of sediments obtained after cavitation treatment of mine water are presented.

Keywords: Risk Management, Reagent-free Treatment of Mine Water, Mobile Technological Complex, Multi-agent Modeling, Decomposition, Laboratory Bench, Mobile Technological Complex Group Management

1. Introduction

Specificity of technological process of extraction of pyrite ores is formation of liquid wastes - acidic polluted waters: drainage and infiltration - in the western literature called acid mine drainage (AMD). The waters are the main suppliers of heavy metals to the environment. Environmental damage from AMD discharges into surface watercourses in the Ural River basin is estimated at several tens of billions of rubles per year. In addition to the costs of compensating for environmental damage, the enterprises incur losses due to the loss with the discharge of some valuable components. The main genetic types of deposits, the exploitation of which generates WACs, are deposits of ores of non-ferrous metals and coal. Typical provinces of deposits development are pyrite deposits of the Urals (Russia), Iberian belt (Spain), USA, Canada, Japan, and lignite basins of Pennsylvania (USA). Ultra-acidic waters with pH from 0.5 to 3.5 occur at all the above sites, when the overwhelming part of the dissolved metals are in the form of free uncomplexed ions, the most dangerous for biota. Specal danger is posed by AMD with a high content of compounds arsenic, typical, for example, for Japan and Hungary [10]. "The existing analogue of the proposed technology is neutralization of AMD with caustic lime. This technology does not provide the required level of purification of mine waters and is associated with high material costs.

There is a known project by Siberian Federal University [18] "aimed at water treatment using cavitation. However, the proposed technology requires the use of recirculation of treated water, which significantly limits its use."

Known hydrodynamic water treatment unit (GDVU-03), developed by the Institute "Tomskagropromtechproekt", designed for water disinfection and purification of water from dissolved heavy metals, salts and other impurities without the use of chemical reagents. The unit implements a method that uses in complex physical and chemical processes occurring in a moving stream of water for water treatment: aeration, cavitation (cold boiling), collapse, coagulation. During these processes, the transfer of dissolved substances in water into insoluble and their removal takes place [13]. The disadvantage of this method when it is necessary to treat large volumes of wastewater is the need to use large areas for equipment. Note that so far we can not solve the problem of purification of acid mine water from heavy metals and their neutralization using reagentless methods on an industrial scale.

2. Materials and Methods

The task of risk management of the introduction of reagentless treatment of acid mine water is aimed primarily at the implementation of the paradigm of minimizing the "environmental-economic" risks of closing unprofitable copper-zinc-copper-ore mines [8]. The solution of the problem is based on a system decomposition of the object, tasks and research criteria. The object of the analysis are large volumes of heterogeneous flows of mine water, coming for treatment. Flow contains very fine particles, up to colloidal ones, sedimentation rate of which is insignificant, they can stay in water for a long time, which is explained not only by small initial particle mass, but also by the absence of spontaneous coagulation (non-slip with each other due to the presence of similar electric charges on their surface). The main ones are: acid-alkaline index (pH), mineralization and its composition, water structure, redox potential. Concentrations of almost all rare-earth elements (REE) in mine waters of the pilot object (Levikhinsky mine) are dozens of times higher than the industrial content. The means for solving this problem is the mobile technological complex (MTC) designed by our team, "operating in the flow-through mode».

It allows to purify water "from heavy metals to the requirements for water of fishery value; to neutralize RWC; to get rid of fine particles contained in the treated water; to return into production or use for other useful purposes the substances contained in the extracted sediments. MTC is designed for round-the-clock operation in conditions of varying mine water discharge and its physical and chemical characteristics. The operation of these complexes is envisaged without service personnel. The complex is designed to operate reliably in conditions of non-stationary character of change of hydrochemical parameters of mine water and possible failures of equipment. A characteristic is simultaneous presence in mine water of heavy metals and sulfates. The complex of problems to be solved is received by decomposition method. Criteria for the problem to be solved are: specific power, kWh/m^3; specific resource and energy consumption, g/m^3 (reagents) and kWh/m^3 (energy); specific production cost of treated water, rubles/m^3; specific operational costs, rubles/m^3. Thus, the task is multi-criteria. We introduce a vector of criteria f0 c f01, f02,..., f0n. To search for the optimal value of f0 it is necessary to determine the order relation, that is the rule of comparison of two vectors, by which we may conclude which one is the best. A criteria convolution procedure is required. Before performing criterion convolution, it is desirable to allocate from the set D of the vector of desired variables a subset Dp found such that for any reasonable definition of the convolution method the solution belongs to this subset. We will refer to reasonable methods of convolution of criteria such that a vector f0 is considered better than f'0 if all components of these vectors, except for the i-th, coincide and f0i> f'0i. "As a complex quality criterion we take the minimum cost of performing MTC tasks with a given probability. The search for a solution to the problem is performed in a class of technologies belonging to the class of AOP (Advance Oxidation Processes), which represents a set of methods allowing the production of natural oxidants (primarily hydroxyl radicals) in the volume or on the surface of water, participating in the removal of impurities in water treatment and disinfection processes carried out inliquids using thermodynamically non-equilibrium state of the liquid medium and "methods of hydrothermocavitation occurring at the interfaces of the phases in the studied medium. The problem is solved by activation of mine water using high-capacity pumps-homogenizers-hydrodynamic cavitators and extraction of heavy metals in ionic form (up to 99%), operating at low water temperatures, and ensuring water purification at pH=3-6 and using catalysts already contained in the waste water. Increased interest to the reagent-free methods of treatment of liquid media is explained by the fact that these methods of cleaning and disinfection do not pollute the natural environment with chemicals and do not have a harmful or irritating effect on the human body. Methods of continuous on-line monitoring of reliability and safety of facilities are becoming more and more relevant due to the need to develop operational prevention technologies, for which methods of monitoring of technological parameters become a priority. The choice of technical solutions must be made under conditions of uncertainty, which is determined by: - trends in time of contents of non-ferrous metals and rare-earth elements (REE) in WAC; - variations in dynamics of sludge accumulation after neutralization and clarification of water in settling ponds; - variations in market share of products obtained from metals contained in WAC; - changes in payments for environmental pollution (EP) [6, 35-42]. Note that the sediments extracted during water treatment of copper-zinc-pyrite mines are the only industrial raw materials for obtaining many rare elements (selenium, tellurium, indium, etc.), as at very low content of these elements in polymetallic ores direct extraction is economically unprofitable. Achieving these goals requires a multiple reduction in the time of chemical processes. Management of the mobile technological complex is aimed at ensuring the required quality of mine water treatment with minimum energy consumption and high operational reliability. The listed functions can be realized in different ways. Choice of method of purification of mine water is determined by physical and chemical composition of water, as well as the requirements of economy, safety on the basis of technical, economic and sanitary-ecological justification. Such a study requires the creation of a stand [5, 340-343]. Currently, water purification and conditioning are carried out using processes of coagulation, sorption, filtration, flotation, ion exchange, regulation of salinity, pH, composition of dissolved gases. All these processes are implemented using different methods: chemical (input of coagulants, flocculants, oxidants, pH regulators, etc.), electrochemical (electrodialysis, electrocoagulation, electrolytic production of sodium hypochloride), physical (ultrasound, ultraviolet irradiation, high voltage spark discharge treatment, mechanical (settling, aeration, filtration, cleaning in hydrocyclones) [9, 327]. The projected BWW treatment complex provides for the installation of mobile technological complexes at all mines belonging to the Lyovikha ore field and being on "wet" conservation (the territory of Kirovograd district of Sverdlovsk region). In the valley of the Tagil River there are several worked-out copper-pyrite mines, these are Lomovsky, Karpushinsky, Belorechensky and Levikhinsky. The treated mine waters are discharged into the Tagil River, where the Lenevskoye water reservoir is located, which is one of the sources of water supply for the city of Nizhny Tagil (population 350 thousand people). At present, the method of neutralization of acid water with lime milk (or lime solution) is used, which both in our country and abroad is the most common method of treatment of large volumes of waste water. Deposition of metals in mine water occurs in the form of hydroxides in settling tanks and at the bottom of artificial ponds. This is a direct loss as these metals are eliminated from service. Approved discharge of mine water of closed Levikha mine is 1300 thousand m^3/year. Mine water of Levikha is a weak sulfuric acid solution having pH~2.5-2.75. The degree of purification of mine water of the flooded Levikhinsky mine reaches 94% for iron and copper. However, below the discharge of purified mine waters into the Tagil river excess of maximum permissible concentrations (MPC) for water bodies of fishery significance has been noted for copper and zinc (80 times), manganese (12 times), iron (8 times), sulfates (4 times) [16]. The discharge of untreated or insufficiently treated wastewater is the main cause of environmental emergencies caused by the accumulation of pollutants. The projected infrastructure of the automated complex of mine water treatment includes: pumping stations (pumping water from mines); mobile technological mine water treatment complexes; brightening pond that receives treated water, and a system for collecting highly dispersed metal powders extracted from the treated water. The complex of mine water treatment includes: automatic control system (ACS) of well pumps, system of interlocks and protections, as well as the system of technical water accounting. The system is used to provide information support to operating personnel, specialists and managers, automatic control of operation of equipment of a well, from which mine water is pumped, makes possible to set parameters of automatic mode, and also allows to switch on (switch off) a well pump remotely from automated working place (AWP) of a mine water treatment complex control manager. The main requirements, imposed to the designs of mobile complexes are high quality of functional indices, reliability, noise immunity, strength, rigidity, manufacturability, efficiency, low values of material capacity and consumed resources. "Mobile technological complexes are equipped with water and energy meters with IoT-radio modules as part of the manufacturer's design, or existing on-site meters can be connected via industrial IoT-modems. All information about the consumption of resources online is transmitted to a specialized software platform that processes, stores, manages data, sends alarms in emergencies and displays analytical data in the dispatching center. Multi-agent modeling is used to design the system, integrating multiple applications that interact through input and output data streams [7]. "For systems of this type, agent-based modeling is a more versatile and powerful approach because it can account for any complex structures and behaviors."

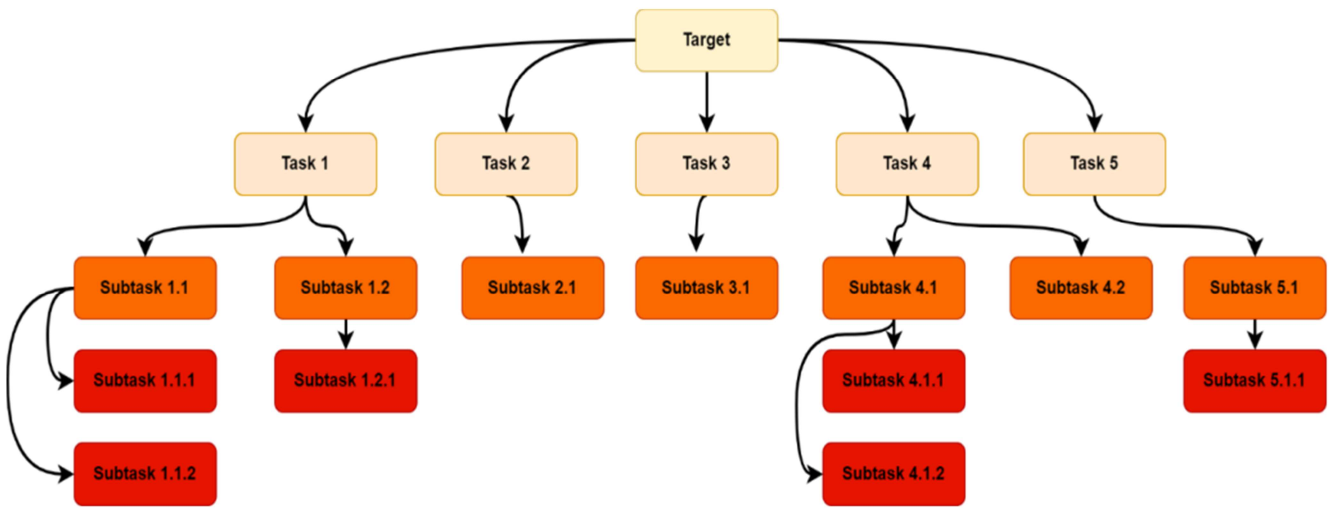

Figure 1. *Decomposition of the objective (compiled by the authors).*

The first task is to determine the sequence of stages and their conditions for purification of AMD and obtaining nanopowders of metals from them to create a highly efficient, environmentally friendly and not requiring complex equipment technological complex. The task of structural-parametric synthesis of a mobile complex of mine water treatment is solved on the basis of a system analysis of treatment processes of AMD in the mobile technological complex. The task is set on the basis of theoretical and experimental research of the main units of the mobile technological complex, marketing research of realization of highly dispersed metal powders obtained by purification of mine water. Marketing research forms the requirements to the recoverable sludge. The formation of sulfates and sulfuric acid from iron sulfides occurs in the process of AMD formation:

$$FeS_2+3{,}5O_2+H_2O \rightarrow FeSO_4+H_2SO_4$$

$$2FeSO_4+H_2SO_4+0{,}5O_2 \rightarrow Fe2$$

$$FeS_2+ Fe_2\,(SO_4)_3+2H_2O+3O_2 \rightarrow 3\,Fe_2\,(SO_4)_3+H_2SO_4$$

Subtask 1. 1 is to determine the forms of total iron content in mine water: bivalent (free (suspensions FeS, $FeCO_3$, $Fe(OH)_2$), dissolved (Fe^{2+}, $FeOH^{+}$); in complex form (mineral and organic complexes); trivalent (free (suspensions, $Fe(OH)_3$ and other sediments), mineral and organic complexes; suspended particle content in mine water; ionic strength of the solution (the measure of the intensity of the electric field created by the ions in the solution) and the pH of the environment, electrical conductivity and dissolved oxygen content in the water, the saturation of water with calcium sulfate; determine the pair Fe (II) $+SO^{2}_{4}$, which ensures the activity of water as a leaching solution (if the iron is in the form of $FeSO_4$ sulfate the aeration of water does not allow for its deferrization hydrolysis of dissolved iron salt produces acid, which lowers pH of water to less than 6.8 at the same time hydrolysis process almost stops); dielectric properties (tangent angle of dielectric losses tg δ and relative dielectric permittivity ε') of emulsion, which characterize its behavior in an external field. On Figure 2 the results of X-ray phase analysis of sediments received after cavitation treatment of mine water are resulted. Sample "0" is the filtered sediment of mine water. Many small peaks can be seen on the X-ray image, which indicate amorphous compounds in the water. There are no narrow peaks at all, which confirms the almost complete absence of crystal lattices. Almost all water is in colloidal state or in the form of fine dispersed suspension (colored yellowish-brown water, the sediment does not fall out even with prolonged sedimentation). There is a small amount of FeO (in dissolved form, divalent iron, clear colorless water) in the total peaks [5].

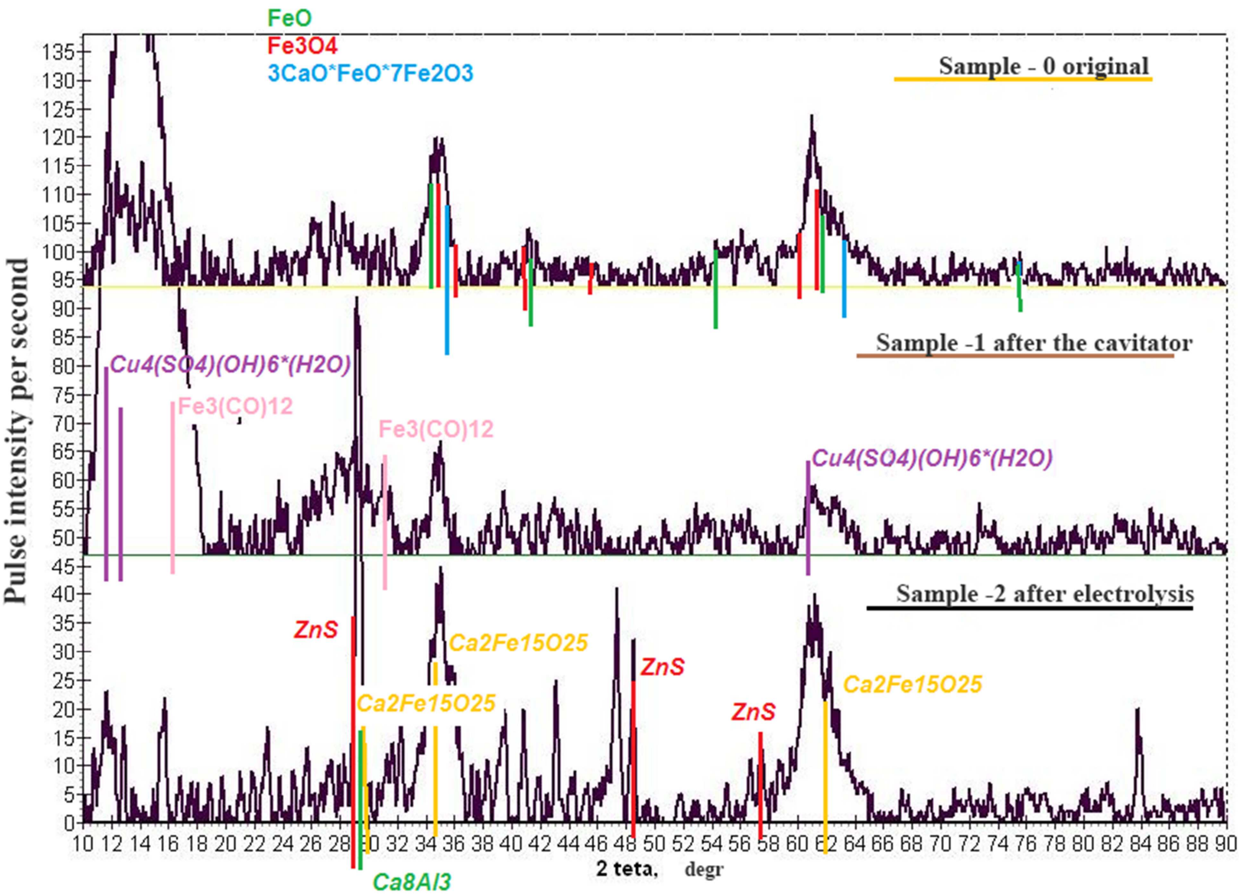

Figure 2. *Results of X-ray phase analysis of sediments obtained after cavitation treatment of mine water [5].*

In the undissolved form Fe_3O_4 (tetravalent iron, transparent water with a brownish-brown precipitate or pronounced red flakes). The program also clearly identifies the compound $3CaO*FeO*7Fe_2O_3$. Sample "1" - filtered sediment after the cavitator (10 passes). On the radiograph not much has changed in the peaks. Only the first peak was much wider and more intense. The compounds changed a lot, there appeared $Fe_3(CO)_{12}$, $Cu_4(SO_4)(OH)*6(H_2O)$. Sample "2" - filtered deposit after electrolysis. At the X-ray film sharp narrow peaks and corresponding compounds ZnS, $Ca_2Fe_{15}O_{25}$, Ca_8Al_3 appeared. Sample- 2CCP (sediment after two cavitators, collected in hydrocyclone as sands). At the X-ray film sharp peaks of high intensity 2θ = 25 deg. and = 31 deg. appeared (highlighted in green). These peaks correspond to Fe_3S_4 compounds. The sample - 2KCP-M (the magnetic fraction was extracted from the previous sample). The sharp lines of high intensity 2θ = 11deg, = 21deg, = 29deg appeared on the XRF. (highlighted in red). These peaks correspond to FeS_2 pyrite. The compound has more than 82% pyrite - this corresponds to the large peak at 11 deg.

Subtask 1.2 consists in modeling of apparatuses of technological complex. A computational experiment with ANSYS Fluent package (Multiphase Flow Model: Mixture in Implicit) Turbulence Models: Stress-BSL (GEKO) Mass Transfer: Cavitation, Schnerr-Sauer Model) was performed to define parameters of cavitator. The Rayleigh-Plesset cavitation model implemented in ANSYS CFX requires parameters such as average bubble diameter and saturated steam pressure to be specified. The bubble radius at the end of compression Rmin is usually in the range 10^{-7} -10^{-8} m with an initial radius R0=1×10^{-6} m. Thus, the volume of the bubble changes by at least 1000 times, which causes the extreme concentration of energy initially stored by the bubble. The main diameter of vapor bubbles (Main diameter) in the Rayleigh-Plesset equation was chosen as 2×10^{-6} m, the saturated vapor pressure (Saturation Pressure) considering the simulated liquid temperature as 15°C (Pn = 3170 Pa).

The second task provides static optimization of control of a group of mobile technological complexes. For a specific technology of mine water treatment, the state of the mobile technological complex at the upper hierarchical level is characterized by the value of unit costs for the treatment of 1 m^3 of mine water and the extraction of metal-containing sediment from it, which are calculated by the formula:

$$S(x)=\sum_{r\in R} S_r(x_r)+\sum_{r\in R}\sum_{\omega\in\Omega} pr^{\omega} S_r^{\omega}(x_r, y_r^{\omega}) \qquad (1)$$

where pr^{ω} is the probability of the outcome;

$y^{\omega}=x^{\omega}-x$ - deviations of the actual mode from the design mode;

$S_r(x_r)$ - estimated costs in the r-th element of the system.

It is reduced to minimization of treated water batch share (batch corresponds to the volume of water treated per shift) by defining control action vector (U) under constraints on the hydrogen index (η) and residual metal concentration in treated water (Cost):

$$\eta \geq \eta^*, \text{Sost} \leq C^*\text{ost} \qquad (2)$$

Permissible range of solutions is determined by the found regulating characteristics and restrictions imposed on the quality characteristics of treated water: Taking into account the uncertainty due to the errors in the estimation of the characteristics of the treated water, the constraints (2) take the form:

$$\eta+\rho(\varepsilon)*S\eta \geq \eta^* \qquad (3)$$

where η*=6,5; ε- allowable probability of violation of restriction on hydrogen index; ρ(ε)- parameter, depending on distribution law f(η) and magnitude ε (at ε=0.95, ρ(ε)=2).

The optimization problem is written in the form:

$$r(U)\rightarrow \min \Omega, \text{ fi } (U)=0 \qquad (4)$$

Losses due to the appearance of a batch of treated water, with disturbed quality characteristics, are calculated by the formula:

$$P=Zp/(V(T)*(l-r(T)), \qquad (5)$$

where Zp is the cost of mine water treatment related to one hour of operation of the technological complex; d is the share of defect; V is the hour productivity of the technological complex in treated water. The optimized parameters must satisfy the conditions of their possible variations: (U) values of output variables with values of input variables [12]. Sub-task 2.1-Identification of adjustment characteristics.

The third task of detecting the degradation of technological equipment, leading to downtime and unscheduled repair costs, is solved using neural networks. The subtask 3.1 is the use of the DSM-method, which allows to extract new knowledge from the results of performed experiments. The name of the method comes from the initials of the English philosopher, logician and economist John Stuart Mill. Before starting the DSM-method, we assume that there is already a certain knowledge base - a database of facts. Strictly described procedures based on inductive logic are applied to the facts from the base, giving at each step a set of formulas, called hypotheses. They are included in the knowledge base. They replenish the initial fact base: Fact Base ⊂ Knowledge Base [1]. Since installations are designed to work in "non-operator" mode, the formation of events (system, warning and emergency) also falls on the complex server. For this purpose a special module was developed, which operation is based on fuzzy logic. This module is connected to output layers of neural networks, which diagnose the work of measuring devices. On the basis of the knowledge laid down during the development, the fuzzy logic module generates output signals about the state of and, if necessary, places it in the message panel for the operator. Sub-task 3.1 - formation of alarms.

The fourth task is to recreate an objective and accurate picture of the occurrence and development of the accident at the entire set of facilities affected by the accident, in a unified chronological format.

The fifth task is aimed at elimination of information leakage, risk of penetration into technological process regulation, elimination of possibility of data destruction or substitution in the system.

The proposed system integrates the concept of security and the concept of extracting high value.

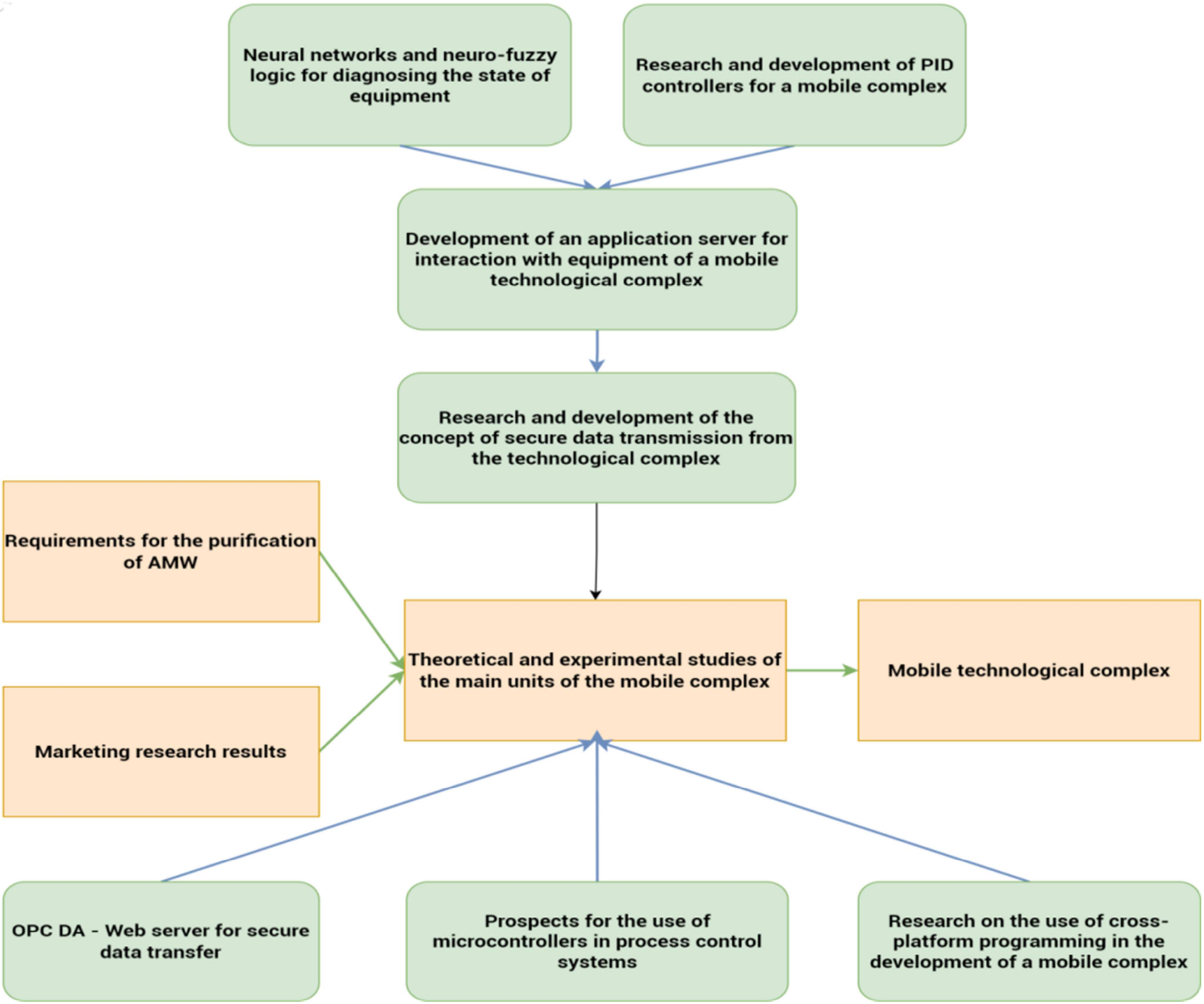

Figure 3. *Mobile technological complex as a projected system (compiled by the authors).*

3. Results

The performed specification of the task of minimizing the environmental and economic risk and the research conducted at the test bench allowed to substantiate the step-by-step programs of the technological process, to estimate the resources required for the production and implementation of the mobile technological complex; to form technical specifications for individual devices, as well as for information and software. Risk management is based on the system decomposition of the object, tasks and research criteria, and made it possible to substantiate the requirements for the MTC, which is characterized by high operational reliability. The experiments carried out on the test bench allowed us to verify the hypothesis about the conditions of occurrence of developed cavitation. Flow-through static cavitators with self-suction effect from 5% to 15% were designed, manufactured and assembled in the bench. The elements of the projected control system of acid mine water treatment without reagents are developed and introduced: PTK_Registrator, PTK_Integrator - software and hardware complexes based on the Prototype package and used for working off the technology of data collection and processing.

4. Discussion

Annually about 15 thousand tons of copper, the same amount of zinc, about 40 thousand tons of iron and significant amounts of antimony, mercury, manganese and other metals are lost with acid mine water at enterprises engaged in mining and processing of copper-pyrite ores [2].

At the stage of searching for solutions with the proposal to use reagent methods of treatment, their main drawback was revealed - for 1 kg of excreted salt it is necessary to use almost as many additional chemical reagents. At the same time, additional costs were required for special concrete structures to ensure water treatment regimes [3]. It has been established that during the formation of mine water development of copper-zinc-pyrite deposits, especially mine water, sulfates and heavy metal ions are added to their composition. This occurs as a result of oxidation of pyrite minerals in the aeration zone after the stripping of the ore body and the formation of soluble sulfate surfaces. This chemical composition characterizes the conditions of intense sulfuric acid leaching, in which the underground flow is formed within the boundaries of the surface catchment area. The form of zinc extraction from sulfate solutions largely depends on both the acidity of solutions, redox conditions, and the concentration of sulfate ions. In the The zinc precipitates predominantly as ferrite in an equilibrium state. Conducting the process in the ferritization mode makes it possible to bind both zinc and iron at the same time. This mode is preferable for metal extraction in mine and tailings water treatment schemes because it does not introduce additional contaminants into the flow.

It was found that in the range of values typical for acid mine waters depending on acidity and iron-oxygen ratio, copper in the equilibrium sediment is in the form of ferrite, hydroxosulfate, cement copper and oxide [17] Zinc goes to sediment in the form of ferrite, and selective precipitation and separation of zinc from copper with formation of insoluble zinc-containing compounds is thermodynamically most probable under oxidizing conditions at pH of equilibrium solutions above 5.2 and Eh 0.57 - 0.60 V and sulfate concentration less than 0.045 mol/dm^3. The theoretical mass fraction of zinc in the selective precipitations obtained in the optimal parameter ranges from 6.28 to 11.78% when converting the phase composition to elemental composition.

«Electrocoagulation and electrocoagulation have a huge number of drawbacks, the main of which are the following: difficulties in servicing electrocoagulators due to clogging of interelectrode space, which needs to be cleaned with scrapers; necessity to maintain a ratio between steel chips and coke, inconvenience of loading, necessity of thorough filtration from finely dispersed phase, consisting of coke particles and iron oxides; - both methods require a huge quantity of chemicals (for reduction of one chromate ion they require a lot of time). Very many methods of waste management are associated with the introduction of chemicals into wastewater solutions and raising pH to values at which the solutions precipitate hydroxides of heavy metals. Sludge from hydroxides of heavy metals and reagent impurities is sometimes disposed by sintering it with glass and firing it with ceramic mass, because without treatment of sludge when pH changes, heavy metals go to mobile forms, polluting the environment. Unfortunately, it is known that there are no reliable self-purification mechanisms for heavy metals in principle» These elements only redistribute from one natural reservoir to another [11]. The main disadvantage of industrial wastewater treatment methods is that eventually new wastes are generated, such as heavy metal hydroxide precipitates, which must also be disposed of.

5. Conclusion

Minimization of the risk of implementation of reagentless treatment of acid mine water is achieved by solving the structural-parametric problem of MTC synthesis. In this case the "reference" variant of MTC structure is determined by physical and chemical properties of mine water, the requirements to the treated water and the existing base of technological units. The methodology of risk management of the project of creating a technology of reagentless treatment of acid mine water proposed in the article allows, in the presence of a priori information to determine the likelihood of achieving the ultimate goal of the project and effectively manage the achievement of this goal, influencing the resources involved. The practical significance of the research lies in the fact that its results make it possible to proceed to the design of a demonstrative prototype of a mobile technological complex providing reagent-free water treatment and neutralization as well as extraction of heavy metal ions from acidic mine waters. Research must be continued.

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