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COMBINED PURIFICATION OF COAL MINE METHANE AND MINE WATER BY THE GAS HYDRATE METHOD TO PRODUCE HYDROGEN

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Abstract. This study demonstrates the technology of the combined purification of mine water and mine methane through the utilization of gas hydrates; purified methane is to be subjected to plasma pyrolysis. Given the considerable variability in the flow rate and concentration of methane, the objective was to identify a viable methodology for the utilisation of mine gas wherein the volumetric quantity and component composition of the gas would not be restrictive parameters. The proposed approach involves the transformation of coal mine gas into a hydrated form. The combination of a coal mine methane-air mixture with mine water to form hydrated gas facilitates the dual objectives of utilizing coal mine gas and desalinating mine water within a single technological process, thereby yielding pure methane, drinking water, and dry salts as final products. Collectively, these advancements enable the generation of new beneficial products, promote the comprehensive development of coal deposit resources, and markedly mitigate the deleterious effects on the environment. A chemical analysis of mine water was conducted, revealing significant mineralization levels that categorize the mine water as saline and underscore the imperative for desalination. The properties and chemical composition of mine methane gas taken from surface degassing wells were analysed. The analytical data indicate that the composition of coal mine methane is close to natural gas, with notable homologues including ethane and propane. The gas mixture is also characterized by the presence of nitrogen (1.69–4.65%), as well as lesser quantities of oxygen (0.08–0.29%) and carbon dioxide (0.19–0.40%). Further analysis of the data reveals fluctuations in methane concentration under varying operational conditions of the wells throughout their functional lifespan. The extracted methane is optimally suited for utilization as a precursor in the generation of what is termed ‘turquoise’ hydrogen, applying the technology of steam-plasma pyrolysis. We delineate various strategies and methodologies that could be employed to harness substantial volumes of mine water and gas from coal deposits for the production of hydrogen fuel, desalinated water, and technical salts as resultant products. The resultant water, possessing adequate quality, is anticipated to avert the contamination of aquatic ecosystems with dissolved mineral salts. Potential beneficiaries of the combined processing technology of mineralized mine water may encompass coal enterprises, joint-stock companies, and, in the foreseeable future, entities within other extractive industries.

Keywords: gaseous hydrate, desalination, methane, mine wastewater, hydrogen, plasma.

1. Introduction

During the extraction of underground minerals, a large amount of mine, quarry and drainage water (hereinafter referred to as mine water, MW) is discharged to the daytime surface. In the coal industry, the specific volume of MW is on average 1.8 m^3/t of extracted coal, which exceeds the water consumption for industrial and household needs by 3–4 times. The formation of MW, especially during underground mining, occurs mainly due to the underground waters of aquifers that mine workings open up, and the feeding lower aquifers that feed them. On the territory of Ukraine, the content of mineral salts in MW reaches 20–30 g/dm^3. The problem of treatment and processing of mineralized water correlates with the interests of the population in large areas of the country's coal-producing regions, being one of the main obstacles to ensuring environmentally safe living conditions for people. In general, in the coal industry, the share of MW with high mineralization (> 1 g/dm^3) is now about 30% of the total volume [1–3].

The mineralized MWs are still used in the industrial water supply for mines and related industries, and are mainly discharged into natural water bodies [4]. The maximum permissible concentration (MPC) of salts in water bodies set for objects of fisheries, domestic drinking and cultural water is 1 g/dm^3. In addition, the MPC is set for some cations and anions (Na, K, Ca, Mg, Fe, Cl, SO_4, etc.). The discharge of mineralized MW has a detrimental effect on the flora and fauna of water bodies, and prolonged exposure leads to their salinity. Wastewater treatment plants operating at coal industry enterprises are not designed to remove dissolved mineral salts from the MW, and special methods and technologies known in the world practice to reduce the mineralization of natural and wastewater, their desalination and demineralization are not widely used in continental conditions. In this regard, the problem of mineralized MW purification at mining enterprises, in particular in the coal industry, is very relevant and has an important scientific and practical significance.

Currently, the main raw material for the production of hydrogen is natural gas. Its safe transportation under high pressure over long distances through main pipelines or in the form of liquid is mastered by all the leading gas-producing countries of the world. Natural gas contains expensive hydrogen, the use of which is economically justified in the production of ammonia, oil refining, and metallurgy when the cost of production allows for maintaining the stability of the hydrogen market. The use of hydrogen as an environmentally safe fuel is unprofitable due to its high cost, and the complexity of safe transportation, which requires its use at the production site. At the same time, the use of hydrogen can increase the efficiency of power plants by up to 65–80% when using fuel cells [5].

The dynamics of natural gas prices demonstrate their instability and upward trend, which requires the search for an alternative source of hydrogen production [6]. Coal mine methane (CMM) is a related product of coal mining, which complicates it and creates dangerous working conditions for personnel. With the largest reserves of CMM among European countries in Ukraine, its production and processing have not become massive. This is due to the complexity of its extraction technology, great depths of occurrence and other production factors. Experience of the O.F. Zasyadko Mine demonstrated that the cost of electricity obtained from CMM is significantly lower even than nuclear electricity [7].

About 50% of the world's hydrogen production is based on vapour–phase reforming of natural gas (in the United States – 90%), and only 4% of hydrogen is obtained by water electrolysis. The purity of the hydrogen obtained in both cases allows it to be used as a raw material for fuel cells [8]. The low cost of electricity obtained from CMM requires its use on-site without connecting to general power-supply networks, where its price increases significantly due to electricity produced by thermal power plants. Reducing the cost of electricity and using it only for water electrolysis processes opens the way to producing hydrogen worth less than $1 per 1 kg and developing the production of solid oxide fuel cells (SOFC) at temperatures below 600 °C [9].

At the same time, the development of technology for SOFC production makes it possible to use as raw materials not only hydrogen but also syngas obtained from

CMM by paroxysmal reforming. SOFC production is constrained by the high cost of initial oxides and the unconventional cycle of their operation. Both problems can be solved by using cheaper electricity produced from methane, and new more efficient technological schemes for the production of zirconium, yttrium, lanthanum, manganese and scandium oxides. The development of the SOFC design makes it possible to reduce the consumption of expensive oxides and increase the service life of the fuel cell and its efficiency by up to 85%. The use of heat generated by solid oxide fuel cells reduces the cost of hydrogen. The development of SOFC production in the world is intensively carried out in the USA, Japan and some European countries [10].

Ukraine, having developed the most modern technologies for producing complex oxides in the form of particles of 10–50 nm, has not yet created an effective model of a fuel cell with a capacity of 1 kW to 1.5 kW. The absence of any efficient SOFC design makes industrial production of hydrogen as a fuel premature. Under these conditions, CMM processing is possible to produce syngas, which can be a raw material for the production of chemical products, primarily methanol, or for the reduction of hematite to magnetite. The problems of using CMM are related to the variability of its concentration, uneven release, and the need to build a chemical and metallurgical complex for its processing at the mining site.

The stability of the composition and volume of CMM should be ensured as an indispensable condition for the operation of any production based on it. The estimated operation of profitable production should be calculated for 20–25 years, taking into account optimal productivity, which is determined both by the availability of affordable and reliable technological equipment and the state of the market [11]. With production of electric energy from CMM, it is possible to consume it on-site for coal mining and enrichment with the support of the state, since otherwise the generated energy must be transferred to the general energy system with a higher price, which will determine the disadvantage of methane production.

Ensuring the combination of safe coal mining and CMM processing processes in a single fuel and energy complex is a strategically important task for the coal industry, which should receive legislative and financial support from the state, especially for state-owned mines. Given the prospects of hydrogen energy, which is intensively developing in the world, it is necessary to provide it with the cheapest and most affordable type of hydrogen-containing raw materials in the form of CMM [12]. At the same time, it is necessary to keep in mind the economic conditions of CMM production, taking into account the service life of existing or newly built coal mines, which have to produce competitive products.

Thus, the presence of existing sources of CMM and its large reserves in the coal deposits of Ukraine makes it promising to develop technological processes for its profitable extraction and processing. The availability of cheap electricity generated from CMM makes it possible to plan the creation of installations for producing cheaper hydrogen, for example, by electrolysis of water. The availability of cheap electricity makes it possible to desalinate MW to reduce their supply to open hydraulic networks. The availability of CMM chemical processing technology makes it possible to start research work on creating pilot plants of various capacities to optimize the parameters of the technology processes and obtain prototypes of commercial products.

This study aimed to research the process of purification of MW and methane using gas hydrate technology, followed by the production of hydrogen. During the study, the following tasks were fulfilled:

- to test gas hydrate technology as a method of methane concentration and desalination of mineralized MW;
- to study the quality of fresh water and to estimate the level of its cost and the possibility of using it in various technologies;
- to design a pilot plant for obtaining methane gas hydrates from model solutions;
- to study the possibility of using a highly mineralized MW for obtaining methane hydrates;
- to study the storage conditions of gas hydrates and the production of pure methane;
- to study the possibility of obtaining salts from MW.

2. Theoretical part

In some countries, reducing the negative impact of mineralized MW on natural water bodies is achieved by using storage ponds with regulated discharge of accumulated MW depending on changes in water flow in watercourses and evaporator ponds that do not have discharge into natural reservoirs and watercourses. Currently, a significant number of scientific and technical developments have been carried out in the world and some experience has been accumulated in the desalination of seawater to obtain drinking water and wastewater from some industries for reuse [13]. It is impossible to transfer these developments and experience directly to the MW for some reasons. Thus, their in-depth study and use in researches are necessary and important.

As a result of the search study, taking into account the existing conditions, the novelty criterion will be satisfied if the results will be based on the:

- study of the chemical composition of mineralized MW to select the most effective and economical methods of desalination (demineralization);
- research of desalination methods to obtain a minimum volume of brine with the maximum salt content;
- search for rational ways to separate brine with the allocation of individual components and obtain marketable products that are in demand.

It is important to organise analytical and experimental research due to the lack of similar studies. At the same time, however, it is necessary to study the technical possibilities for the effective use of foreign developments, their main disadvantage – almost the same amount of additional chemicals must be used per 1 kg of salts to be removed. At the same time, additional costs were required for special concrete structures to ensure water treatment regimes.

The development of a technology for desalination of MW to obtain useful products (salts, etc.) is promising. Although many priorities for technological implementation are assigned to Western countries, almost all promising industrial membrane desalination plants have not been implemented in the industry for various reasons. At the same time, new technological methods of purification (electrochemical and biotechnological) were being developed. However, they could be used only at the stage of water purification to ensure drinking water conditions, and therefore the environmental aspect of the problem, and in particular, the provision of low-waste technology, was almost completely ignored [4].

In any case, the process of water purification with the release of clean water occurs in parallel with the formation of pollution concentrates (sludge, brine), which are potentially hazardous to the environment. This necessitates the greening of technological solutions in the treatment of MW. The prospects for solving the problem lie only in a combined treatment of MW, which makes it possible to obtain a range of products useful for human life: clean drinking water, substances and materials with consumer properties (edible salt, soda ash, magnesium, iron, etc.).

The main types of useful products that can be obtained from MW include:

- NaCl salt, which price varies from $40 to 60 per 1 t, depending on the quality;
- calcium compounds – dry calcium chloride (for the production of building materials), $CaCl_2$ solution (for further production of chalk, for clearing roads from snow), and slaked lime (for the production of building materials);
- magnesium compounds – is in demand on the market at $290 per 1 t of magnesium chloride and $2,500 per 1 t of magnesium metal. Magnesium compounds are widely used in metallurgy (production of aluminium alloys, cast iron, refractories), agriculture (additives to fertilisers and feed), as well as in chemistry, pharmaceuticals, construction materials and mechanical engineering;
- desalinated water; the shortage of fresh water, both drinking and of technical quality, in mining areas makes this product most in demand and valuable.

In Ukraine, there are examples of the development of technologies and designs of plants for the treatment of groundwater from abandoned mines in the Luhansk region [14]. Their aim is to physically and chemically affect mechanical, biological and chemical impurities with the ultimate goal of separating them from water. To separate solid impurities, filters of various designs (gravity, mesh, cartridge, magnetic, membrane, etc.) should be used. For salt purification, a reverse osmosis membrane with a size of up to 1.5 nm is sometimes used, which allows only water molecules and no more than 5% of dissolved salts to pass through. In this case, the quality of purified water meets the standard for the composition of desalinated and disinfected water. Deep purification removes other elements harmful to drinking water (calcium, magnesium, fluorine, sulphur, chlorine).

In practice, the methane/water ratio can be unstable, so the main goal should be to remove as much methane as possible as an efficient energy carrier and a hazardous compound for the environment. Excess MW should be processed using a full range of physical and chemical processes to produce drinking water. One volume of water in the hydrated state binds from 70 to 300 volumes of gases, depending on the size of their molecules. Calculations show that one volume of water can absorb up to 240 g of methane.

The dependence of the degree of subcooling of natural gas at a given pressure was first described in [15, 16]. The essence of the technology is to implement the conditions for obtaining large gas hydrate crystals. The effect of different types of water (cold, melt, distilled, hot) was studied. The best results were obtained from water obtained during the decomposition of the gas hydrate itself. The hydrate formation process is affected by the inhibitors, catalysts and gas impurities that change the chemical potential of the components.

Freshwater produced by hydrate technology is the most promising for use as meltwater. Methane storage in the gas hydrate state requires 5 times less pressure than in the free state – 2–3 MPa and 16 MPa, respectively. The formation and decomposition of gas hydrates in the presence of substances with electronic conductivity increases hydrogen yields compared to water electrolysis [17]. The gas hydrate technology is multifunctional, which makes it possible to use various processes to obtain various products in a single technological space.

3. Results and discussion

The comparative analysis showed that it is advisable to investigate the gas hydrate demineralisation process for MW. Butane, propane, and freons (CFCs) can be used as gas hydrates. However, due to the low availability of some of them and the toxicity of others, it seems very attractive to use CMM for this purpose. If mineralised MW and CMM are used, the water is demineralised, as the resulting hydrate contains only fresh water and gas, and salts remain in solution because their molecules are too large to fit into the cavities formed by water molecules.

An experimental unit for gas hydrate technology of CMM utilisation and MW demineralisation was developed [18]. The tests of the developed unit confirmed the fundamental possibility of carrying out the hydrate formation in a technologically acceptable range of pressures and temperatures. Depending on the size of gas molecules, a framework of a certain structure is formed. The degree of filling of the lattice cavities depends on the pressure, temperature and contact time of the injected gas molecules. Gas hydrates crystallise into two structures (I and II) with lattice constants of 1.2 nm and 1.73 nm, respectively [19]. Each unit cell of structure I consists of 46 and structure II of 136 water molecules. One volume of water in the hydrate state binds from 70 to 300 volumes of gas, depending on the size of their molecules [20].

The main factors that determine the conditions for the formation and stable existence of gas hydrates are the composition of gases, moisture content, phase state, temperature and pressure. The gas composition determines the main condition for hydrate formation – the higher is the molecular weight of an individual gas or gas mixture, the lower is the pressure required to form a hydrate at a constant temperature. Converting CMM to hydrate helps to solve many difficulties associated with its disposal. However, the specificity of the component composition of CMM imposes its requirements for the development of rational parameters of technologies for converting it to a hydrate state [21].

The main kinetic parameters that determine hydrate formation in the water-gas system are as follows [22]:

1. Microscopic kinetics: critical nucleation radius; induction period; nucleation Gibbs energy; interfacial surface tension; activation energy of hydrate formation.
2. Macroscopic kinetics: geometric dimensions; parameters of heat and mass transfer; interfacial surface area; supercooling.

The influence of 'third' substances, such as inhibitors, catalysts and gas impurities, on the hydrate formation process is not taken into account here. The solution to these issues is one of the urgent tasks of gas hydrate physics and consists of the qualitative analysis of experimental data. Hydrate formation from gas mixtures is more complicated than that of individual gases, which is manifested in changes of induction period and the rate of hydrate formation [23].

Experimental data on the equilibrium parameters of hydrate formation from various mixtures of hydrate-forming agents are widely presented in the works of Y.F. Makogon [24, 25]. When a 'third substance' is introduced into the gas-water system, the chemical potential of the components changes and, accordingly, the equilibrium conditions of hydrate formation shift. Strengthening the conditions for hydrate formation by introducing a 'third substance' is called inhibition. Glycols, electrolyte solutions, and alcohols can be used as non-volatile inhibitors, which change the activity of water in such solutions. Non-electrolyte molecules, once in solution, serve as the germs of a clathrate structure similar to a gas hydrate, being located in the cavities of clathrates and almost not interacting with the lattice.

If the hydrate formation process is carried out on CMM using MW, it is necessary to consider the degree of its mineralisation, since the phase diagram of the hydrate formation process in salt water differs from the usual one in that higher pressures and lower temperatures are required for hydrate formation [26]. When the hydrate-forming gas comes into contact with mineralised water, a hydrate is formed, which includes the gas and fresh water, while salts remain in solution because their molecules are too large to fit into the cavities formed by water molecules [27]. This fact is the basis for the use of gas hydrate technology and also for the mineralisation of the MW, which was confirmed by the numerous studies.

If the mine methane-air mixture is used as a hydrate-forming gas, it is possible to desalinate water and utilise mine gas in a single technological process to obtain fresh water, dry salts and pure methane as finished products. This makes it possible to significantly reduce the harmful environmental impact of a mining enterprise, as well as to obtain new useful products [28]. The concentration of CMM by the gas hydrate method requires certain energy costs that need to be calculated. In winter, the MW temperature can be maintained by the natural factor, which will significantly reduce the cost of gas and make it more economically attractive than natural gas. The use of MW instead of drinking water will also reduce the cost of methane.

Chemical analysis of the MW sampled at the Heroyiv Kosmosa Mine of DTEK Pavlohradvuhillya (seam C_9 from the 964th face of the collecting drift) was carried out. The results of the analysis are shown in Table 1.

Table 1 – Results of the mine water chemical analysis

Compound	Content, mg/dm^3
Anions	
Cl^-	19357.34
SO_4^{2-}	1883.08
HCO_3^-	195.20
Total anions	21435.62
Cations	
$Na^+ + K^+$	10269.33
Ca^{2+}	1623.24
Mg^{2+}	262.65
Total cations	12155.22
Microcomponents	
Mn^{2+}	0.56
$Fe^{2+} + Fe^{3+}$	0.38
NH_4^+	7.00
Other	
pH	6.48
Alkalinity, mg-eq HCO_3^-/dm^3	4.59
Hardness, mg-eq/dm^3	29.4
Mineralisation, mg/dm^3	33590.84

The water density at 20°C according to DSTU 7261:2012 equalled 1.025 g/cm^3. The colour of the water according to DSTU 180-7027:2003 was clear. pH (DSTU 4077-2001) was equal to 6.48. The analysis results indicated a significant content of anions – chlorides (49.71%) and the sum of Na^+ and K^+ cations (40.66%). The total mineralisation was 33590.84 mg/dm^3, which classifies the MW as saline water and indicates the need for its treatment.

The brines obtained from MW are raw materials for the production of valuable marketable salts. Their production will reduce the cost of fuel. The use of MW with zero or conditionally negative cost (due to the negative impact on the quality of drinking water after it is discharged into open water bodies) also requires an economic calculation of the costs of reducing the salt concentration from 3–5 g/dm^3 to 0.5 g/dm^3.

The initial data for calculating the technical and economic indicators of the gas hydrate desalination process are:

- composition and quantity of MW;
- composition and quality of the gas containing CMM within 5–25% to create a balance for the production of methane gas hydrates;
- the price of drinking water;

- estimated cost of the available MW (including energy costs for its lifting and desalination to the MPC level);
- the price of salts that can be extracted from brine after methane gas hydrates are produced.
- the price of distilled water for industrial hydrogen electrolysis (evaporation and concentration method).

Minimisation of capital and operating costs to reduce the cost of water to the level of affordability for the population should be ensured by a technological scheme that includes the following processes:

1. Disinfection of the entire water flow by ozone, ultraviolet, etc. methods.
2. Removal of iron and manganese using gravity, disc or other filters with a hole diameter of 3 μm to 100 μm.
3. Partial desalination and disinfection of water at the baromembrane plant.
4. Mixing of different water streams to achieve the required water quality.

These processes create a three-stage sanitary and epidemiological protection of water. An industrial plant should provide a capacity of up to 500 m^3/h with a payback period of no more than 10 years at a price that corresponds to the drinking water tariff. Providing the population with drinking water will allow them to preserve industrial enterprises and social infrastructure and, on this basis, to start using treated desalted MW to produce hydrogen by electrolysis.

CMM and mineralised MW are by-products of coal mining. MW treatment requires significant energy consumption. For example, the efficiency of the desalination process does not exceed 10% (reverse osmosis) with highly mineralised brines formation. The gas hydrate desalination method has a higher efficiency (up to 26%).

Coal mine gas has a large variation in methane concentration and flow rate. The gas produced from the massif contains 98% methane, but its flow rate is also variable. Estimates of methane reserves in the Donetsk region alone have shown the presence of 2.5 trillion m^3 of CH_4.

CMM can be used in the following processes:

1. Combustion in boiler houses at a methane concentration of ≥30% to produce cheap electricity and heat.
2. Production of methane from mixtures with a CH_4 concentration of ≥85%.
3. Combustion in gas turbines with a methane concentration of ≥1.6%.
4. Production of motor fuel by compression of methane at a pressure of 25 MPa with a methane concentration of >95%.
5. Use in internal combustion engines as a fuel at a concentration of >6% to produce cheap electricity.
6. Conversion of methane into a solid state (gas hydrate) in a wide range of methane concentrations (≤40%).

The main preparatory process in the technology is the production of methane gas hydrates for the purification of the MW and methane itself for further hydrogen production by plasma pyrolysis. Typical properties and chemical composition of

CMM from surface degassing wells (according to the data of MakNII and IGTM of the National Academy of Sciences of Ukraine) are shown in Table 2.

The data analysis shows that the composition of CMM is close to natural gas. The gas mixture also contains nitrogen (1.69–4.65%), oxygen (0.08–0.29%) and carbon dioxide (0.19–0.40%).

Table 2 – Chemical composition and some properties of surface degassing wells and natural gas

Well location	Chemical composition, %							Physical properties	
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	O_2	N_2	CO_2	Density, kg/m^3	Calorific value, kcal/m^3
Glyboka mine	94.5	0.52	0.01	–	0.08	4.65	0.24	0.746	8480
O.F. Zasyadko mine	95.2	2.19	0.44	-	0.29	1.69	0.19	0.747	8905
Natural gas	95.1	1.10	0.30	0.1	0.1	2.90	0.40	0.748	8726

The results of experimental studies on methane production from the abandoned areas 1 and 2 (wells MT-323 and A-3351) of the O.F. Zasyadko Mine (according to the data of the Institute of Geological and Technical Research of the National Academy of Sciences of Ukraine) are presented in Table 3.

Table 3 – Methane concentration from degassing wells in various modes

Operating mode	Gas mixture flow rate, m^3/min		CH_4, %	
	MT-323	A-3351	MT-323	A-3351
I	4.86	6.3	92	83
II	5.66	6.9	83	83
III	0.9	7.1	1.0	83

The data analysis shows a change in methane concentration under different well-operating conditions during their operation.

The composition of gas recovered from wells at different sites is shown in Table 4.

Table 4 – Composition of gas recovered from different wells

Well	Composition, %					
	He	H_2	CH_4	CO_2	O_2	N_2
MT-323	0.085	0.024	92.0	-	0.04	1.6
A-3351	0.13	0.002	83	2.5	0.4	13.9

The results of chemical analysis of CMM samples indicate the presence of impurities, primarily nitrogen. It is necessary to study the process of cleaning the CMM and MW using gas hydrate technology. To do this, the following tasks need to be fulfilled:

1. To test the gas hydrate technology as a method of methane concentration and desalination of mineralised MW.
2. To study the quality of fresh water to estimate its cost and the possibility of using it in various technologies.

3. Create a pilot plant for the production of methane gas hydrates from model solutions.

4. To study the possibility of using highly mineralised MW for the production of methane hydrates.

5. Study the conditions of storage of gas hydrates and production of pure methane.

6. To study the possibility of salts obtaining from MW.

The M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine is developing a method for producing hydrogen from CMM under the influence of plasma energy [29–33]. The schematic diagram of this process is shown in Fig. 1.

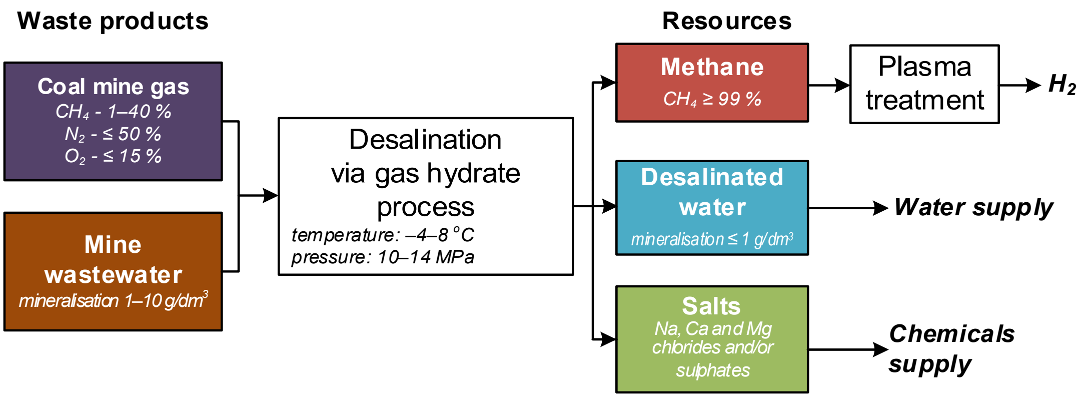

Figure 1 – A flow-chart of gas hydrate desalination technology applied to coal mine wastes

The implementation of the research results should provide an additional source of fresh water to meet the domestic drinking and production needs of mining towns and villages. Also, the purified water can be used in the process of electrolysis production of hydrogen in the conditions of the surface complex of the mine. The water produced must be of appropriate quality to prevent contamination of water bodies with dissolved mineral salts. Consumers of the technology of combined processing of MW may include coal-mining companies, joint stock companies, etc., and in the future – enterprises of other mining industries. The first step in implementing this technology should be the construction and testing of a pilot plant for the combined utilisation of MW and CMM at one of the mines in the Western Donbas or Lviv-Volyn basin.

4. Conclusion

1. The solution to the problem of highly mineralised mine water treatment is in line with the interests of the population in large coal mining regions, being an important condition for ensuring safe living conditions. Given the shortage of drinking water in rural areas, Ukraine's state policy should provide the funds for combined processing of highly mineralised mine water, as well as prevention of insufficiently treated water discharge.

2. Gas hydrate technology uses the property of gases to fill molecular cavities in the crystal lattice of water at certain pressures and temperatures, forming a solid compound – a gas hydrate containing gas and water. Using gas hydrate technology, it is possible to utilise CMM and demineralise MW in a single technological process, and in the future, to extract rare elements from brines.

3. The novel technological scheme for the production of hydrogen from CMM is proposed. The main preparatory process in the technology is the process of obtaining methane gas hydrates for cleaning CMM and MW for further hydrogen production by plasma pyrolysis of methane and/or electrolysis of purified water. The proposed scheme allows for low-waste production of demineralised water, considering the requirements for environmental safety in mining regions.

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СУМІСНЕ ОЧИЩЕННЯ ШАХТНОГО МЕТАНУ ТА ШАХТНОЇ ВОДИ ГАЗОГІДРАТНИМ СПОСОБОМ ДЛЯ ОДЕРЖАННЯ ВОДНЮ

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Анотація. Роботу присвячено технології спільної переробки шахтних вод і шахтного метану із застосуванням газогідратів, а також піролізу метану із застосуванням плазмових технологій. У зв'язку з великим коливанням дебітів і концентрації метану постає завдання знайти такий спосіб утилізації шахтного газу, для якого кількість і компонентний склад газу не був би жорсткою умовою. Таким способом є переведення шахтного газу в гідратний стан. Використання як газу гідратоутворення шахтної метаноповітряної суміші та шахтної води дає змогу в єдиному технологічному процесі здійснити утилізацію шахтного газу та опріснення шахтної води з отриманням як готових продуктів чистого метану, прісної води і сухих солей. Усе це в комплексі дає змогу отримати нові корисні продукти, здійснити комплексне освоєння ресурсів вугільного родовища та істотно знизити шкідливий вплив на навколишнє середовище. Проведено хімічний аналіз шахтної води. Результати аналізу вказують на суттєву мінералізацію, що відносить шахтну воду до солоних вод і вказує на необхідність її знесолення. Проаналізовано властивості та хімічний склад шахтного газу метану з поверхневих дегазаційних свердловин. Аналіз даних свідчить, що за складом шахтний метан близький до природнього газу. Наявність його гомологів перш за все етану та пропану. Також у газовій суміші присутній азот (1,69–4,65%). В меншому ступені присутні кисень (0,08–0,29%) та діоксид вуглецю (0,19–0,40%). Аналіз даних також свідчить про зміну концентрації метану при різних режимах роботи свердловин при їх експлуатації. Отриманий метан найдоцільніше використовувати як сировину для отримання так званого «бірюзового» водню за технологією пароплазмового піролізу. Запропоновані методи і способи, за допомогою яких можливо утилізувати багатотоннажні відхід вуглевидобутку – шахтні води і газ, з отриманням як кінцевих продуктів водневого палива, опрісненої води і технічних солей. Отримана вода належної якості дозволить запобігти забрудненню водних об'єктів розчиненими мінеральними солями. Споживачами технології комплексного перероблення мінералізованих шахтних вод можуть бути вугільні компанії, акціонерні товариства тощо, а в перспективі – підприємства інших гірничодобувних галузей промисловості.

Ключові слова: газовий гідрат, опріснення, метан, шахтні води, водень, плазма.