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Utilization of coal mine brines in the chlorine production process

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Abstract

Utilization of coal mine saline waters is regarded as the most appropriate method of solving the ecological problems created by these waters in Poland. One of the methods of utilizing the most concentrated saline waters — called coal mine brines, which is presently being considered — consists in using them for chlorine production in a diaphragm electrolysis process. On the basis of investigations a technology for preparing mine brine for diaphragm electrolysis has been developed. The process consists of purification of brine with a high magnesium ion concentration while obtaining, as a by-product, magnesium hydroxide and bringing the brine to the state of saturation using sodium chloride from the catholyte evaporation process. The technology has been verified on the diaphragm electrolysis experimental installation. It offers low energy consumption and waste-free operation.

Keywords: Coal mine brines; Chlorine production; Diaphragm electrolysis

1. Introduction

Poland is one of the poorest countries in Europe with respect to fresh water resources. The average annual amount is as little as 1700 m^3 for one inhabitant with the European being 4800 m^3. The Vistula River contains about 55% of the total fresh water resources in Poland and covers about 35% of the water needs in the country, together with the river basin — about 60%. Unfortunately, for many years excessive salt concentration has been found in the Vistula, reaching the 354th km of its course. In dry years even in Warsaw the Cl$^-$ concentration in the Vistula is over 0.4 g/l.

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The main source of the Vistula River salinity is chlorides contained in waters from hard coal mines: these constitute as much as 94% of the chlorides drained to the Vistula, Warsaw included, and about 62% over its total course. The Vistula River salinity is the cause of losses in industry, agriculture, water transport and municipal administration. The magnitude of these losses is estimated to be 100–250 million USD per year [1].

Mine waters are divided into four groups depending on the sum of chloride and sulfate ions. The most noxious group of mine waters is the so-called mine brines (group IV) of chloride and sulfate ions concentration over 42 kg/m^3, which in the Vistula River basin constitute 7.0% of the volume of the drained waters, but carry as much as 56% of salt load. Low salinity mine waters (group III) of 1.8–42 kg/m^3 concentration constitute 28% of the total water volume and carry 43% of the salt load.

2. Concepts for solving the coal mine water problem

The concepts for solving the saline water problem considered so far can be divided into three basic groups:

- controlled drainage of waters (hydrotechnical method)
- recirculation and forcing of waters into the rock mass
- utilization

The controlled drainage of waters consists in their switching over by a system of pipelines and batching them into rivers in periods of high water levels through a system of storage reservoirs. This requires high capital investment and also creates a secondary environmental hazard due to the possibility of saline water infiltration to underground waters. With the drawbacks mentioned above, the hydrotechnical method offers only an appeasement of the problem, and thus it is treated as an auxiliary method of local significance [2,3]. The recirculation method consists in forcing of saline waters under high pressure into the drained water-bearing complex through previously made bore holes [2,4]. The forced water is subject to partial recirculation and flows again to mine workings, partially migrates in the opposite direction creating in the water-bearing formations a hydraulic barrier, restricting the in-flow of waters from further parts of the rock mass. The recirculation method is used in the United States [5]. It requires careful geological recognition and cannot be used in places where forcing of waters may contaminate drinking water or lead to an out-flow of water in undesirable spots. Also considered are the forcing and storage of water in a Cenomanian formation deposit [2]. This deposit is characterized by high porosity and a possibility of storing large amounts of water is foreseen. However, there are no experimental data on this subject.

The utilization of saline waters consists of their use in processes in which chemical compounds are obtained to be used in economy and as water for industrial and municipal purposes. The utilization of mine brines (group IV), in general, takes place in one stage. The utilization of low salinity waters (group III) takes place in two stages where, in the first stage, the waters are concentrated to the levels corresponding to group IV.

In view of the above-mentioned facts, in the situation in which hydrotechnical methods are only of local importance, the possibilities of recirculation are not known, and this method can be used only in some of the mines. Only the use of coal mine saline waters offers a reduction of chlorine ions concentration in the Vistula to a satisfactory level. As a result of the data mentioned before, even the utilization of a small volume of mine waters from group IV can give over two-fold reduction of salt discarding to the Vistula.

Due to the disastrous ecological situation in the south of Poland where mines discarding waters of the greatest salinity are found, the following requirements are made of the utilization technologies:

- complete utilization of all the components occurring in mine waters to obtain valuable products while using inexpensive and available raw materials
- low energy consumption

The main product of the utilization in the discussed technologies is sodium chloride which is also the principal component of saline mine waters. However, because of the complex composition of saline waters, achieving a suitable quality of the sodium chloride obtained and separation and utilization of the remaining components of these waters poses a serious problem.

So far, only one utilization technology has been implemented in a larger scale in the country: in the Underground Water Desalination Plant of the Debiensko coal mine, the technology for obtaining evaporated salt, gypsum and desalted water, developed by the Main Mining Institute, was used. The technology is unique in the world scale and its application for over 10 years confirmed the aptness of the accepted technological and apparatus solutions. However, in the present form the installation cannot be duplicated because of the small unit productivity of the evaporators, necessitating the batching of expensive sodium sulfate in order to remove calcium in the form of calcium sulfate, obtaining utilization products of inferior quality and large quantities of post-crystallization lyes requiring further treatment. The salt produced contains a relatively large amount of magnesium since magnesium ions are not removed from the brine subjected to concentration.

The installation for utilization of the saline waters from the Debiensko and Budryk coal mines [6] now being started up is based on the latest achievements in the field of the evaporation of untreated mine waters, calcium sulfate removal, heat exchange and minimization of energy consumption. A disadvantage of the installation is the exclusive use of the most expensive form of energy, i.e., electric energy and the unsolved problem of post-crystallization lye utilization.

Considered at present is a possibility of using a few technologies in which preliminary purification of particularly magnesium ions is employed. It is suggested to use phosphoric acid for magnesium ion removal with a concurrent obtaining of multi-component fertilizers or fodder components or calcined dolomite with the use of which magnesium hydroxide is obtained [3]. Sale of the utilization products mentioned might be ensured; however, fertilizer technology results in secondary ecological hazards, and when using calcined dolomite, calcium ions are introduced into the brine which causes technological problems and makes calcium chloride utilization necessary.

3. Chlorine production from coal mine brines

Preliminary tests on the suitability of mine brines for obtaining chlorine were carried out in Poland already in the 1960s. The suitability of these brines for chlorine production by the diaphragm method, after concentration to the state of saturation and purification by the standard method, was found. Also the suitability of the salt from catholyte evaporation in diaphragm electrolysis process for mercury electrolysis [7,8] was demonstrated. The suitability of the evaporated salt obtained from mine brine by the method developed by the Main Mining Institute for chlorine production by the mercury method was also found [9].

In recent years in the Institute of Inorganic Chemistry and Technology of the Silesian Technical University, investigations on the application of the brine from the Ziemowit coal mine for chlorine production were made.

The utilization of coal mine brine for chlorine production requires bringing the concentration of the particular components up to the values conforming with the requirements referring to brines for electrolysis. Due to the fact that the membrane method of chlorine production calls for the use of rock or evaporated salt, only the application of the diaphragm method for the mine brine utilization was considered.

Brine for diaphragm electrolysis should contain: NaCl, at least 310 kg/ m^3; Ca^{2+}, at most 5 g/m^3; Mg^{2+}, at most 1 g/m^3; and NH_4^+, at most 10 g/m^3. The composition of the brine from the Ziemowit coal mine is presented in Table 1. Sodium chloride concentration is nearly three times lower than the required one, whereas the calcium and magnesium ion concentration is many times higher. Also the ammonium and sulfate ion concentration, which is harmful to the electrolysis process, is substantial as well as the bromine and iodine ion concentration, which has a negative effect on chlorine purity.

Table 1
Composition of the mine brine

Component	Concentration, g/m^3
Na^+	38,840
Ca^{2+}	2,520
Mg^{2+}	2,840
K^+	650
NH_4^+	20
B	11
Cl^-	68,060
SO_4^{2-}	2,780
HCO_3^-	76
I^-	6
Br^-	201

4. Laboratory testing

The aim of the first stage of testing was to obtain brine fulfilling the requirements of electrolysis with minimum input of energy and reagents. Attention was also paid to the possibility of utilization of waste products produced in the process of brine purification.

At first, purification of the brine of calcium and magnesium ions by a method commonly used in chlorine industry, i.e., by treatment with natrium hydroxide and natrium carbonate, was considered. Mine brine of the composition presented in Table 1 was saturated with rock salt. Brine of the following composition was obtained: NaCl, 315 kg/m^3; Ca^{2+}, 2.69 kg/ m^3; and Mg^{2+}, 3.10 kg/m^3.

Purification was carried out at the temperature of 40°C. The suspension was subjected to sedimentation in thermostated cylinders. After 24 h thickness of the sediment was measured and related to the initial height of the suspension column was assumed to be the sediment volume. Then filtration ability of the sediment was tested by the vacuum method at negative pressure of $0.4 \cdot 10^5$ Pa. Dense, narrow pored filter paper was used. The results of brine purification are given in the Table 2. In the same table are the results obtained in the case of the natrium hydroxide and natrium carbonate method with 20% recirculation of the suspension and with recirculation and addition of flocculant. The flocculant Bozefloc A 42 was used in the form of a solution of 0.1% concentration in the amount of 0.1% in relation to precipitate mass. It was found that due to the low rate of sedimentation and high volume of the very poorly filterable precipitate, the purification of brine by addition of NaOH and Na_2CO_3 is unsuitable for the purification of coal mine brine. Thus, it was thought advisable to investigate the possibility of two-stage purification of mine brine with a by-product of magnesium hydroxide.

Four variants of preparing mine brine for electrolysis were worked out which differed in the method of obtaining the required sodium chloride concentration (Fig. 1). In variant I the brine is saturated with rock salt. In variant II

Table 2
Purification of the saturated brine

Purification method	Sedimentation rate, mm/h	Sediment volume, %	Filtration rate, kg/m^2 • h	Filter cake humidity, %
NaOH and Na_2CO_3 addition	57	38.5	0.9[a]	52.6
As above with recirculation	176	18.2	2.8	50.1
As above with flocculant	227	15.2	2.7	47.4

[a]At the beginning of the filtration the filtrate was turbid (about 6 ml).

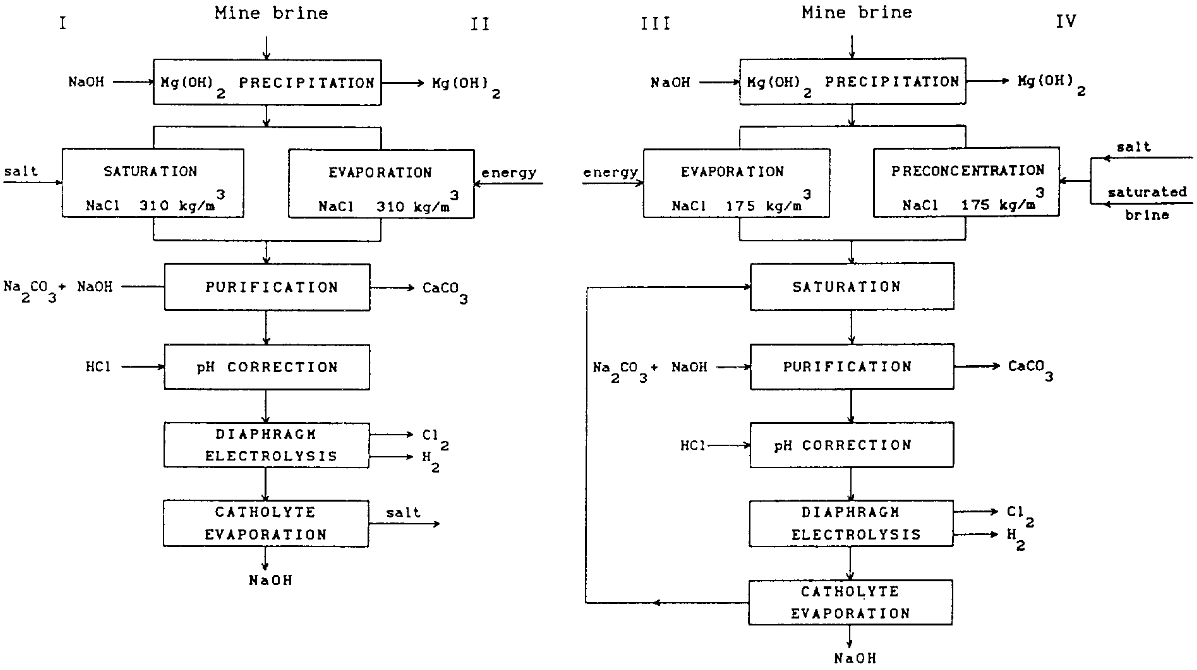

Fig. 1. Variants of mine brine preparation for electrolysis.

the brine is thermally concentrated. The most advantageous for energy reasons, as well as on account of the possibility of utilization of high quantities of salt from mine waters, are variants III and IV in which the brine is first evaporated or preconcentrated to about 175 kg/m^3 concentration and then additionally saturated with salt from catholyte evaporation. Obtaining salt from catholyte evaporation is a characteristic feature of the chlorine diaphragm method production. The solution described above has been patented [10]. Especially beneficial is variant III since it does not require external salt supply (contrary to variants I and IV), ensuring the utilization of large amounts of salt from mine waters while using much less energy than in variant II.

Testing was also made on electrodialytic concentration of coal mine brine, treating such concentration as an alternative to the thermal one [11].

A serious research problem was the separation of magnesium hydroxide from mine brine. For magnesium hydroxide precipitation in industrial processes, calcined dolomite, burnt lime or ammonia are most often used. However, the precipitating substances mentioned above cannot be used to precipitate $Mg(OH)_2$ from mine brine when the brine is handled for chlorine production since significant amounts of calcium ions are introduced together with calcined dolomite or burnt lime. Their precipitation at the second stage of purifying would require increased amounts of soda and this would increase the amount of waste sludge. Moreover, due to high calcium and sulfate ion concentration in coal mine brines, introduction of additional calcium ions may result in precipitation of calcium sulfate whose presence in magnesium hydroxide would exclude its use for refractories production. When precipitation by ammonia would be applied, ammonium might remain in brine. Ammonium ions are very dangerous in the electrolysis process since they form explosive nitrogen trichloride. Thus, the maximum allowable ammonium ion concentration in brine used for electrolysis is 10 g/m^3 [12].

Due to the reasons presented above, precipitation of magnesium hydroxide from coal mine brine can be carried out only when using sodium hydroxide. However, the use of NaOH as a precipitating agent creates substantial difficulties since the suspension obtained sediments very slowly and the final sediment is difficult to filtrate.

On the basis of our own studies, a new method of precipitating magnesium hydroxide has been proposed. The so-called forming of the sediment was used in this method resulting in higher degree of $Mg(OH)_2$ crystallinity. The investigations concerning this method have been described in more detail in a separate publication [13]. The magnesium hydroxide is then flocculated and dewatered.

The brine from the Ziemowit coal mine, after removing the magnesium ions, was thermally concentrated to 175 kg/m^3 NaCl concentration and then saturated to 315 kg/m^3 concentration in accordance with variant III of the preparation of mine brine for electrolysis (Fig. 1), which was found, as it was mentioned before, to be the most advantageous one. As a result of the concentration, the brine of the composition was obtained (Table 3). The catholyte evaporation salt composition which would have been obtained in the diaphragm electrolysis process of such concentrated and then saturated brine was calculated on the basis of diaphragm electrolysis model [14] and the data from the installation for catholyte concentration in the chlorine production plant in the Wloclawek Nitrogen Works. The following catholyte evaporation salt composition was assumed (%): NaCl, 93.45; Na_2SO_4, 3.49; NaOH, 0.20; H_2O, 2.80. The brine was saturated with simulated salt of the composition given above; after crystallization of calcium sulfate, which was carried out at 45°C for 6 h, the brine of the composition given in Table 3 was obtained. The brine was purified by the addition of NaOH and Na_2CO_3. Since a small amount of magnesium ions has a beneficial effect on the course of brine purification, accelerating the clarification of the solution, magnesium chloride solution was added to the brine to achieve 20–100 g/m^3 magnesium ion concentration. The results of the purification are presented in Table 4, which also includes the results of the vacuum filtration of the sediment.

Table 3
Composition of the brine evaporated and saturated according to variant III

Brine	Concentration, kg/m^3			
	NaCl	Ca^{2+}	SO_4^{2-}	NaOH
Evaporated	175	3.98	4.35	0.32
Saturated with salt from catholyte evaporation	318	1.85	3.52	0.64

Table 4
Purification of the brine

Mg^{2+} concentration in brine, g/m^3	Ca:Mg ratio	Sedimentation rate, m/h	Sediment volume, %	Composition of purified brine					Results of sediment filtration		
				kg/m^3			g/m^3		Rate $kg/m^2 \cdot h$	Filter cake humidity, %	NaCl content
				NaCl	Na_2CO_3	NaOH	Ca^{2+}	Mg^{2+}			
20	92	2.31	0.85	307.4	0.45	0.55	4.5	0.9	410	23.8	10.8
40	46	9.44	1.25	–	0.44	0.49	4.2	0.5	340	23.5	10.5
60	31	10.91	1.52	–	0.45	0.42	4.7	0.6	250	26.1	12.2
80	23	7.16	1.85	–	0.43	0.37	4.5	0.0	135	28.7	14.0
100	18	5.18	2.25	–	0.44	0.30	4.8	1.0	75	32.5	16.7

5. Testing in the experimental installation

Tests in the experimental installation of the Ziemowit coal mine were carried out according to the scheme presented in Fig. 2. In relation to laboratory tests, the sequence of operations was changed, i.e., first the brine was preconcentrated with salt from catholyte evaporation and then it was evaporated. With such a solution it is easier to remove calcium sulfate. The advisability of this change results from the experience of the Main Mining Institute from the above-mentioned installation of brine utilization in the Debiensko coal mine. Calcium sulfate is removed in the course of brine evaporation in the first stage of evaporators at 120°C.

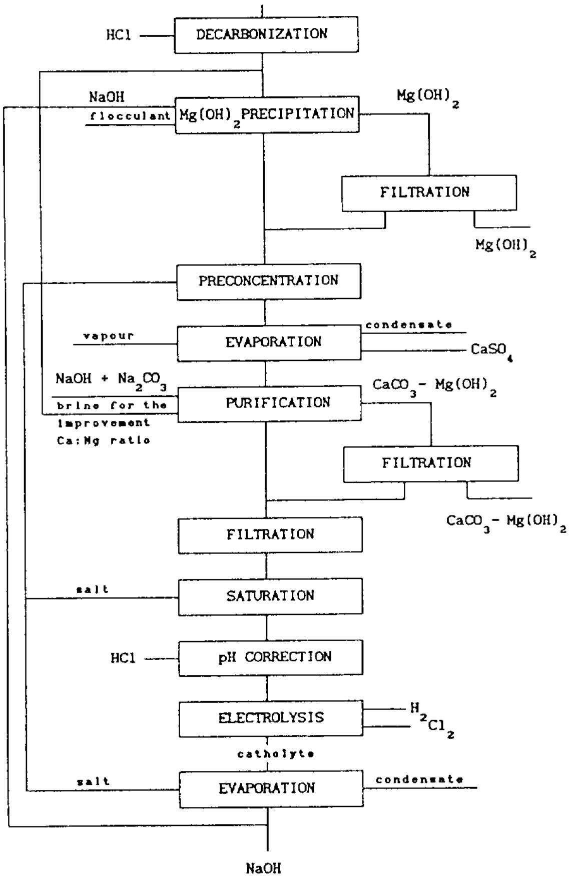

Fig. 2. Schematic diagram of the process of chlorine production from mine brine in the experimental installation.

In the experimental installation tests were made on the preparation and purification of mine brine for many months in a continuous process of diaphragm electrolysis, and samples of by-products were prepared to examine their usability. The electrolysis was carried out in the POLEL-3 kA electrolyzer which is a reproducible element of the industrial POLEL-30/50kA. The composition of the brine from the Ziemowit colliery during the tests in the experimental installation is given in Table 5.

The mine brine was decarbonized by acidifying with hydrochloric acid and blowing with compressed air. Then, magnesium hydroxide was precipitated while investigating both the periodic and the continuous process. The precipitated $Mg(OH)_2$ was subjected to flocculation and then dewatered. Dewatering of $Mg(OH)_2$ was tested in a filtration centrifuge, settling centrifuge, diaphragm press and continuous filter press. As an example, the results of sediment dewatering in a continuous belt filtration press are presented (Table 6). Due to the fact that the filter cake is very compact for its repulpation to wash $Mg(OH)_2$, an installation based on a jet-centrifugal mill concept was used. Low humidity of the filtration cake

Table 5
Composition of the brine from Ziemowit coal mine; tests in the experimental installation

Component	Concentration, g/m^3
Na^+	34,500 - 37,800
Ca^{2+}	2,360 - 2,680
Mg^{2+}	2,630 - 2,800
K^+	430 - 900
NH_4^+	4.1 - 23
B	9.3 - 15.1
Cl^-	64,240 - 70,950
SO_4^{2-}	2,740 - 3,050
HCO_3^-	815 - 976
I^-	5.3 - 10.2
Br^-	95 - 230

obtained in the case of dewatering in a belt filtration press makes it possible to obtain chloride content of the desired level with a small dosage of washing water. In the case of washing through a single repulpation of the filter cake of 41% humidity to NaCl content 5%, 2.5% and 1%, the consumption of washing water was (kg H_2O/kg $Mg(OH)_2$): 1, 3, 9, respectively. With twice-repeated repulpation, the NaCl content equal to 1% is obtained with the washing water dosage 3 kg/kg $Mg(OH)_2$. The small dosage of washing water is essential on account of recirculation of the washings to the process, and the related necessity of evaporating an additional amount of water.

The brine devoid of magnesium ions was preconcentrated with salt from catholyte evaporation from diaphragm electrolysis and then evaporated to saturation. During the evaporation, calcium sulfate precipitated and was removed. In Table 7 the composition of the brine devoid of magnesium ions and of the preconcentrated and the evaporated brine in presented.

Then the brine was purified by adding NaOH and Na_2CO_3. In order to obtain a favorable concentration ratio of calcium ions to magnesium ions, during purification, magnesium ion containing mine brine, i.e., raw decarbonized brine in the amount of 20 dm^3/m^3 was added to the brine; the concentration ratio of calcium ions to magnesium ions was about 50:1. The sedimentation rate of the suspension during final purification was about 7 m/h, and the volume of the precipitate after 24 h of sedimentation 1.7-2.1%. The calcium carbonate precipitate obtained at the time of final purification of the brine was dehydrated by vacuum filtration at negative pressure of $0.4 \cdot 10^5$ Pa, and also in a filtration centrifuge, settling centrifuge and plate-and-frame filter press. In Table 8 the results of sediment dewatering by vacuum filtration and in a filtration centrifuge and plate-and-frame filter press are presented. On account of brine dilution which takes place during the purification process, it was again saturated with salt from catholyte evaporation and after correction of pH subjected to diaphragm electrolysis. Diaphragm electrolysis, carried out for 18 months, did not present any difficulties which could be caused by improper purification of the brine.

As a result of the electrolysis, chlorine, hydrogen and catholyte — the latter being a solution of sodium hydroxide and sodium chloride — were obtained. Catholyte concentration yielded salt, which was recirculated and concentrated solution of sodium hydroxide. A part of sodium hydroxide produced was used to precipitate magnesium hydroxide.

In the course of the investigation, samples of magnesium hydroxide were prepared to test its suitability for the obtaining of magnesium oxide for the refractories industry. The tests were made in the Academy of Mining and Metallurgy in Kraków. On the basis of the tests of magnesium hydroxide of various sodium chloride content, the permissible NaCl content in $Mg(OH)_2$ for the production of magnesia clinker for the refractories industry was determined. This is 1% in the case of highest quality magnesia products, 2.5% in the case of good quality products, and 5% in the case of the magnesium-chromium and magnesium-aluminum co-clinkers. Conditions for the processing of magnesium hydroxide from coal brine into the above-mentioned products were selected, and it was found that it is a intermediate product fully suitable for the production of clinkers and co-clinkers in which magnesium oxide is the main component. It was also found that from magnesia derived from coal mine brine clinkers can be obtained which are not inferior in quality as compared to their best equivalents produced elsewhere.

Analytical and vegetative studies of the calcium carbonate obtained on final purification of coal mine brine carried out at the Institute of Soil Cultivation, Fertilizing and Soil Sciences at Puławy have shown great force of

Table 6
Dewatering of the flocculated $Mg(OH)_2$ in a belt filtration press

Belt feed rate, m/min	Filter cake humidity, %	Filtration rate, $kg/m^2 \cdot h$	NaCl con-tent in the dry filter cake, %
0.2	39-40	37.1	7.0-7.3
1.0	41-43	45.9	7.6-8.3

Table 7
Results of brine preconcentration and evaporation; tests in the experimental installation

Brine	Concentration, kg/m^3			
	NaCl	NaOH	Ca^{2+}	SO_4^{2-}
Devoid of Mg^{2+} ions	103-110	0.15-2.80	2.35-2.60	2.70-2.95
Preconcentrated with salt from catholyte evaporation	175-190	0.25-0.55	2.35-2.60	2.06-3.48
Evaporated	320-322	0.63-0.88	3.12-3.37	1.83-3.34

Table 8
Dewatering and washing of calcium carbonate; tests in the experimental installation

Dewatering method	Filtration rate, $kg/m^2 \cdot h$	Filter cake humidity, %	NaCl content in dry filter cake
Vacuum filtration	345	32.9	16.9
Vacuum filtration	137	41.1	1.8[a]
Filtration in the centrifuge	520	22.4	10.0
Filtration in the centrifuge	245	28.8	2.0[a]
Filtration in the plate-and-frame filter press	300[b]	39.7	5.99[c]

[a] Washing with water in the amount of 0.9 kg/kg $CaCO_3$ was carried out; filtration rate was given with consideration to washing time.
[b] Filtrate output is given ($dm^3/m^2 \cdot h$).
[c] Washing with water in the amount of 0.4 kg/kg $CaCO_3$.

neutralization and chemical activity of this compound. The allowable sodium chloride content in calcium carbonate was determined to be 11.3%. A great advantage of the carbonate obtained from coal mine brine is the low content of undesirable components such as silica, metallic trioxides and sulfur, as well as content of heavy metals which is many times lower than the maximum allowable one. Calcium carbonate obtained from mine brine fulfills the requirements for calcium fertilizers.

On the basis of the tests carried out in the experimental installation, the industrial technology of chlorine, hydrogen and sodium hydroxide production from coal mine brine was developed.

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