Recycling of Rock-Salt Dust and Brine after Rock-Salt Production

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Abstract

This paper concerns the issue of the management and recycling of rock-waste (rock-salt dust in particular), tailings, and brine generated by rock-salt extraction and processing. The author discusses the methods of brine treatment for the needs of further processing. In that context, an option for combined rock-salt dust and salt-mine brine recycling has been developed, with the use of the existing installations and with the objective to obtain evaporated salt for commercial purposes. The paper also mentions other options of rock-salt dust and brine management in one of the salt mines belonging to the KGHM "Polska Miedź" S.A. corporation.

Keywords: rock salt, waste rock-salt dust, brine, brine treatment, environmental protection

Introduction

Sodium chloride (NaCl) or salt, as it is generally called, occurs in nature either in solid or liquid forms: rock salt and brine. Salt is also found in seawater.

Rock salt is extracted from the deposits with classical mining methods by rock cutting either mechanically or by blasting. Spoils are delivered to the processing plant to be subjected to mechanical processing (crushing, sieving, dedusting etc.), followed by enrichment, depending on the mineral's designation (e.g. table salt with potassium iodide, road salt with anti-caking agents).

Brine is collected either from the places of its natural occurrence or after it is generated by the rock-mass leaching process. Evaporated salt is obtained through brine evaporation. Evaporated salt can be enriched similarly to rock salt.

In the case of seawater, salt extraction relies on natural evaporation. The process takes place in special ponds, or salt pans, where seawater is subjected to sunshine. In high temperature, salt crystallizes with evaporation.

Regardless of the salt production method, salt can be used for the following purposes:

- edible salt is designed for the food industry and used as condiment for consumption (table salt);
- industrial salt is applied e.g. in power engineering, chemical and paint industries, chemical household products, or electrolysis processes;
- road salt is used for defrosting and winter road maintenance.

Table 1 presents the global salt (NaCl) production by continents (Bilans gospodarki… 2015).

Rock salt resources in Poland

Documented economic geological rock-salt resources amounted to more than 85.4 billion Mg in 2014. The current resource status and the degree of resource recognition and maintenance are presented in Table 2 (Bilans zasobów… 2015).

Rock salt extraction in Poland (Bilans zasobów… 2014)

The extraction of rock salt amounted to 4.19 million Mg in Poland in 2014. A detailed production structure is presented in Table 3.

In addition, 75,100 Mg of evaporated salt was obtained by underground coal-mine brine recycling in the Zakład Odsalania Dębieńsko Sp. z o.o. desalination plant.

Waste generation during salt mining

Dry rock-salt mining generates waste which, on the one hand, reduces the economic result, and, on the other hand, creates a number of problems associated with waste management. We should be aware, however, that mining waste also contains salt with smaller fractions of less than 1 mm (dust fraction). That fraction is hard to sell and that is why the salt mines use it to backfill abandoned underground workings.

Dry rock-salt mining methods are applied in two salt mines in Poland: "Kłodawa" and "Polkowice-Sieroszowice". However, the facilities carry out different methods of rock-mass cutting. In the "Kłodawa" Salt Mine, blasting operations are used (with explosives), while the "Polkowice-Sieroszowice" Salt Mine is using mechanical cutting methods with roadheaders. Either method has its

Tab. 1. Global salt production in 2013 [in thousand Mg]

Tab. 1. Globalna produkcja soli w 2013 roku [w tys. Mg]

Continent	Production
Europa	69 077
Africa	7 960
South America	17 714
North and Middle America	64 493
Asia	110 454
Australia and Oceania	12 292
W O R L D	**280 990**

Tab. 2. Rock salt resources status at the end of 2014 [in million Mg]

Tab. 2. Status zasobów soli skalnej na koniec2014 roku [w mln Mg]

Specification	Amount of deposits	Geological resources		Industrial resources
		Balance sheet	Off-balance sheet	
Total resources	**19**	**85 405.50**	**22 124.69**	**1 769.61**
in that – resources exploited deposits				
Deposits of active plants	6	15 139.69	–	1 769.61
in that – resources undeveloped deposits				
Deposits identified	10	70 077.82	21 937.44	–
in that - the bed in which the operation was abandoned				
Discontinued operation	3	187.88	187.25	–

advantages and disadvantages. The "Kłodawa" spoils are characterized by coarse grains, with a fairly small proportion of dust in the proportion of ca. 5% of the extracted material. Much more salt dust, reaching even 20% of extracted material, occurs upon mechanical cutting (Andrusikiewicz 2012). That proportion is further increased by the dust generated in the processing plant. The "Kłodawa" Salt Mine operates a surface Processing Plant, while the "Polkowice-Sieroszowice" one carries out that operation underground.

In the event of the sale of the excavated material to chemical processing plants, the salt-dust issue is not significant because the clients do not have any specific requirements relating to raw-material granulation. We should, however, remember that road salt is the basic product of the two Polish salt mines. Salt-dust fraction is tolerated in that product, although in a limited proportion. Excessive salt dust must be disposed of. It seems that brine production is the most effective form of salt-dust disposal, with further recycling by evaporation. Thus, evaporated salt is obtained. It can be used for the production of e.g. dishwasher and water softening tablets, licking stones for animals etc. The market analysis indicates that there is a growing demand for such products.

Brine treatment

The brine obtained from rock-salt dissolution (raw brine) is not a pure sodium chloride solution. It contains a number of compounds whose presence is not desirable after the evaporation process. Raw brine is subjected to standard treatment to remove calcium and magnesium compounds because their presence can cause plugging of process equipment and installations. Raw brine may also contain other compounds or elements, e.g. heavy metals. The quantities of heavy metals are strictly controlled in edible salt. Consequently, it is necessary to purify raw brine depending on the later use of salt (Andrusikiewicz and Tora 2012).

Brine preparation involves salt-dust dissolution with min. 96% of pure NaCl content in water. The intention is to obtain brine with the min. of 305 g of $NaCl/dcm^3$ H_2O content.

Tab. 3. The rock-salt extraction structure in Poland in 2014 [in thousand Mg]

Tab. 3. Struktura wydobycia soli skalnej w Polsce w 2014 roku [w tys. Mg]

	Manufacturer	Extraction	Participation %
„Wet” method	Kopalnia Soli „Kłodawa” S.A.	477,0	11,4
	Zakłady Górnicze „Polkowice-Sieroszowice”	294,0	7,0
„Dry” method	Inowrocławskie Kopalnie Soli „Solino”	2 950,0	70,4
	Kawernowy Podziemny Magazyn Gazu Kossakowo	469,0 [a)]	11,2
T O T A L		**4 190,0**	**100,0**

reliminary chemical treatment consists in the precipitation of calcium and magnesium from brine, in the form of hard-to-dissolve compounds. This can be achieved by the application of sodium carbonate Na2CO3 and sodium hydroxide NaOH.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + NaSO_4$$

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2\downarrow + 2NaCl$$

The respective process diagram is shown in Fig. 1.

At the end of the process, calcium carbonate $CaCO_3$ and magnesium hydroxide $Mg(OH)_2$ are obtained as waste substances after chemical treatment of brine. During the treatment process, metals can also be partially precipitated (iron, titanium, molybdenum, nickel, chromium, vanadium, and tungsten). Precipitated impurities are removed by sedimentation, filtration or both. Before removal, the filtration cake is usually compacted either in vacuum filters, with rotational drums, or in centrifuges to obtain the solid content of 50-80%. Purified brine should contain the following: Ca < 2mg/l; Mg < 1mg/l; SO_4 < 5 g/l.

If it is necessary to continue brine purification by secondary treatment. Membrane techniques are applied for that purpose (Andrusikiewicz 2014). Membrane filtration consists in the separation of the feed stream (pre-treated brine is the feed material here) into two final products in the form of permeate: the stream which passes through the membrane (purified brine) and retentate: the stream enriched with the substances stopped by the membrane (brine impurities). The diagram showing the membrane filtration process is shown in Fig. 2.

The membrane techniques are characterized by high chemical resistance of membranes, thermal durability, and long service life. They can be successfully used e.g. to separate the liquid streams in either uniform or multi-phase systems. They are highly competitive in comparison to classical methods owing to low energy consumption and ease of expanding the process scale, which is possible by the use of modular structures (Porębski et al. 2012). Depending on the particle sizes of the components subjected to separation, the membrane processes are categorized in accordance with Fig. 3.

The membrane processes are the following:

– Microfiltration (MF), allowing for the separation of fine suspensions and colloids, as well as some large-particle compounds and microorganisms. In that process, the membrane works as a sieve. MF membrane pore diameters belong to the range of 0.1-10 µm. We can obtain high permeate streams by applying the transmembrane pressure of < 0.2 MPa.

– Ultrafiltration (UF) which is one of the most common separation processes designed to clarify or concentrate solutions and compound fractioning. This process consists in physical sifting of dissolved or colloidal substance particles through the membranes with specific pore sizes (1–100 nm). The separation results depend primarily on the sizes of the particles being separated. The separation mechanism is based on sieving, with 0.1-1 MPa pressure as a drive force.

– Nanofiltration (NF), showing intermediate properties between those of reverse osmosis and ultrafiltration (the NF process is also called the reverse low-pressure osmosis). The drive force in this process consists in the pressure difference (from 1 to 3 MPa) existing on both sides of the membrane. The NF process applies a sieve mechanism of separation, dissolution, and diffusion. Bivalent or higher multi-valent salts are removed in that process, among others.

– Reverse osmosis (RO) is based on the natural osmosis phenomenon. If a membrane separates either the solution from the dissolvent or two solutions representing the same concentration, natural flow of the dissolvent to the solution with

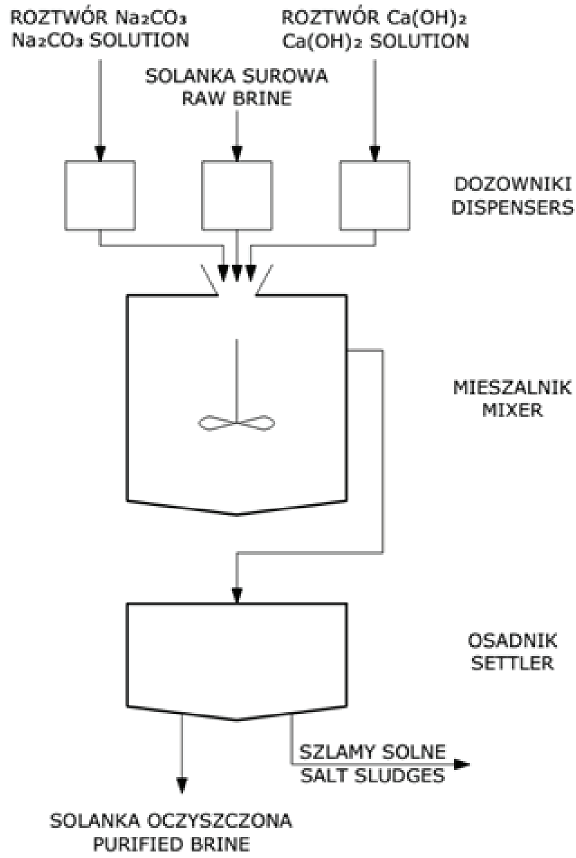

Fig. 1. Process diagram of preliminary brine treatment

Rys. 1. Schemat procesu wstępnej przeróbki solanki

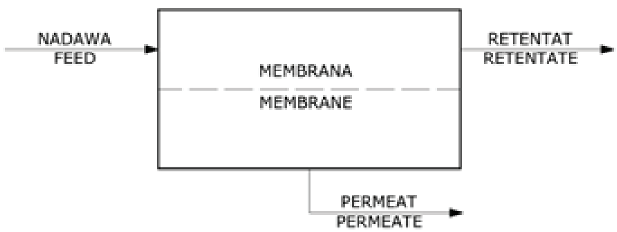

Fig. 2. Membrane filtration process diagram

Rys. 2. Schemat procesu filtracji membranowej

higher concentration occurs. The pressure which balances the osmotic flow is called osmotic pressure. In the event that hydrostatic pressure, exceeding osmotic pressure, is developed on the side of the higher-concentration solution, the dissolvent will penetrate from the higher-concentration solution to the dissolved solution, which is the reverse direction in comparison to that of natural osmosis.

The brine treatment methods presented here are usually adequate in respect of the brine content parameters suitable for further evaporation. Nevertheless, when some metallic elements are identified in brine, it may be necessary to apply other processes. Ione exchange techniques were tested for that purpose. They consist in a selective ion exchange process which causes displacement of specific ions from the liquid being filtrated: metal ions occurring in brine in the case under discussion. Based on the test results, we can conclude that the assumed degree of heavy-metal removal was attained. It was also found that the brine's pH value and metal content at the feed of the ion-exchange station are essential for the effectiveness of that method.

Salt-dust disposal in the "Kłodawa" S.A. Salt Mine

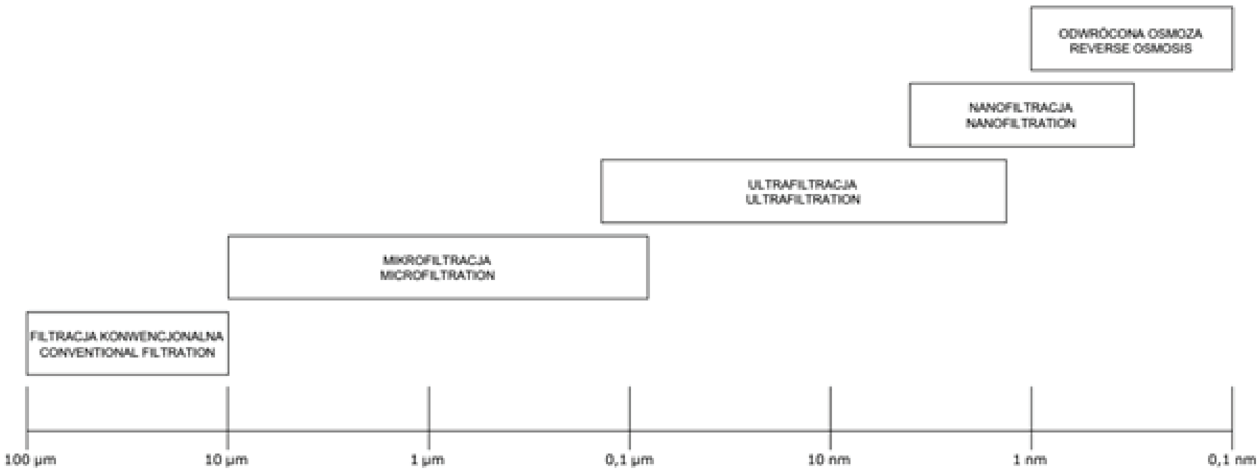

Fig. 3. Scope of filtration in membrane processes

Rys. 3. Zakres filtracji w procesach membranowych

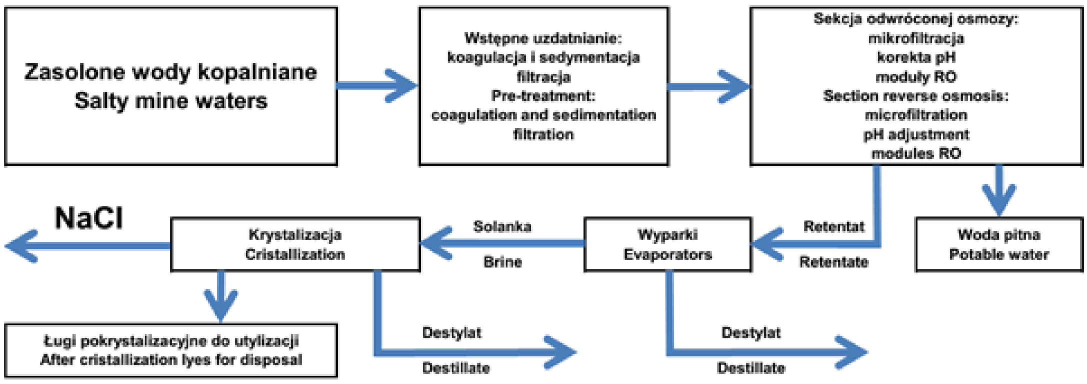

Fig. 4. Installation diagram for desalination of mine waters

Rys. 4. Schemat instalacji do odsalania wód kopalnianych

Salt dust is generated in two locations in the whole salt production cycle: place of extraction (salt working faces) and the processing plant. In the former case, salt dust is rarely transported to the land surface. It is rather used underground, e.g. to level the working bottom, with the excess dumped into abandoned workings or empty chambers. However, problems are created by the dust generated by the processing plants. Such problems are usually resolved by transportation of salt dust to the Dębieńsko Ltd. desalination plant (the company was acquired by the Przedsiębiorstwo Gospodarki Wodnej i Rekultywacji S.A. on 01.07.2015). The plant is designed for coal-mine brine treatment. Collected brine is saturated with salt dust to increase salt concentration. Next, saturated brine is treated by reverse osmosis (Fig. 4) and once concentration reaches ca. 130 g NaCl/dcm^3, the brine is directed to the installation equipped with pressure crystallizers, using saline mist concentration (Fig. 5). Finally, evaporated salt is received, with ca. 99.8% NaCl content. The installation's capacity allows to produce ca. 100,000 Mg of evaporated salt a year, with concurrent purification (desalination) of up to 2.3 million cubic metres of water.

Salt-dust disposal in the "Polkowice-Sieroszowice" Salt Mine

Mechanical rock-mass cutting generates ca. 20% of spoils belonging to dust fractions. Similarly to the "Kłodawa" Salt Mine situation, it is next to impossible to sell that product. Consequently, salt dust has to be dumped into abandoned workings or chambers. Of course, such a solution is negative for economic effects because a considerable portion of spoils is not commercialized.

It seems that the construction of a salt pan can resolve the problem. Such a solution is supported by the following:

– the quantities of mine brine, with high salt concentration (ca. 100 g NaCl/dcm^3 on average),

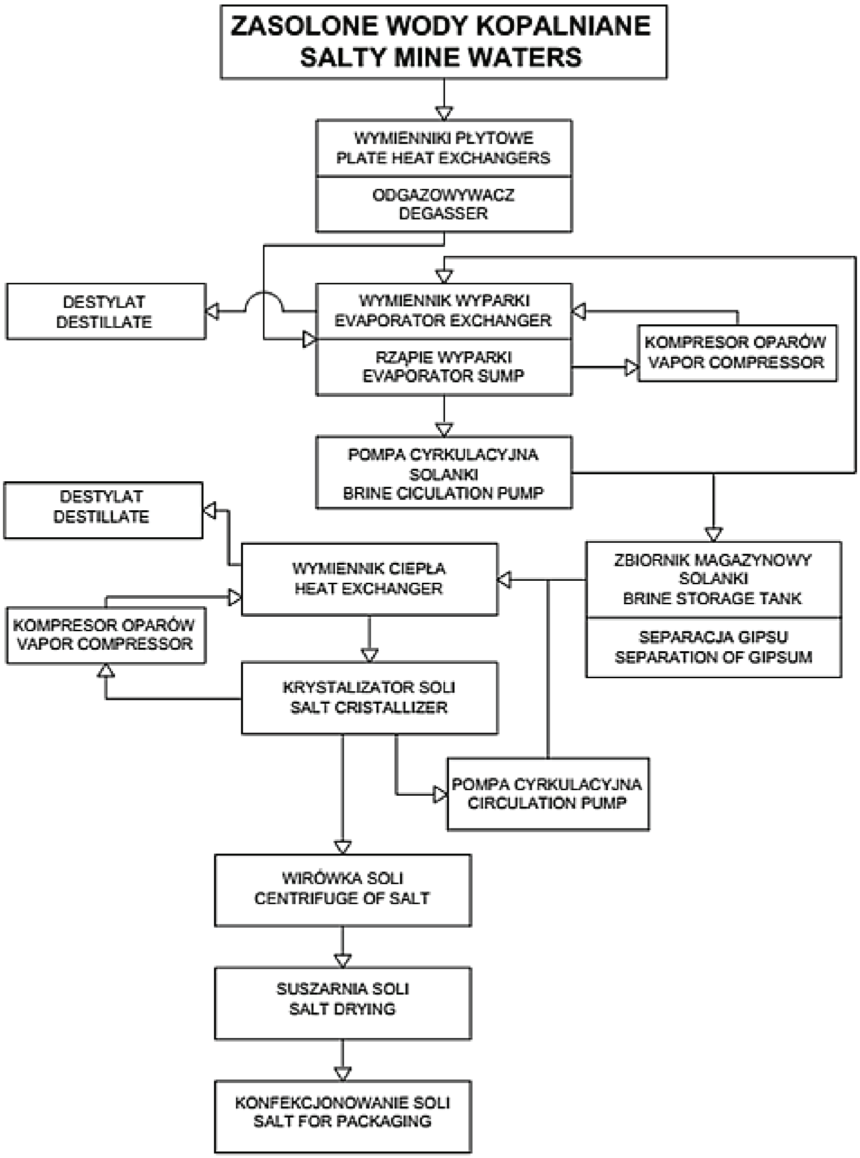

Fig. 5. Installation diagram for the evaporation of the mine water

Rys. 5. Schemat instalacji do odparowania wód kopalnianych

which are presently pumped to the Zakład Hydrotechniczny "Żelazny Most" processing plant;

– the quantities of salt dust; if full mining capacity is reached, ca. 200,000 Mg of salt dust can be generated a year!

Upon selection of a suitable site for a potential mine-brine collection station, ca. 1.15 million cubic metres of water containing ca. 110,000 Mg of Cl– ions, will be available. After mine-brine saturation with salt dust, saturated brine will be available for the recovery of ca. 300,000 Mg of evaporated salt.

A preliminary analysis of the situation in salt mines allowed to contemplate the potential of constructing a brine evaporation installation. Owing to the composition of mine brine, the liquid material will have to be treated by one of the membrane methods specified above. Detailed research should answer the question whether it will be necessary to apply the ion-exchange technology since several metallic elements have been identified in mine brine. Upon treatment, saturated brine should be pumped into the evaporation installation. In that regard, a multiple-effect evaporation installation and an installation with mechanical salt mist compression (Mechanical Vapour Recompression System) were considered, expanded by a multi-effect evaporation (MME) system. Since we are short of adequate quantities of heat, as the medium being indispensable for the installation using a Thermal Vapour Recompression (TVR) system, that type of installation was omitted in our analysis. After a profound analysis of Polish and European evaporated salt markets, it was initially determined that the contemplated capital investment could become profitable within several years.

Conclusion

The issue of salt-extraction waste and tailings disposal represents two faces: economic and ecological. Both are equally important. Reaching a possibly high profit is the purpose of any economic activity, including mining. The recovery of mineral raw materials is associated with certain costs. Consequently, it seems logical that we aspire to sell the whole extracted mineral with profit. Unfortunately, it is not always possible to, as we presented the case of rock-salt dust. On the other hand, ecological considerations are calling for the necessity to dispose of mine brine. Unused rock-salt dust stockpiling and mine-brine dumping into surface watercourses would cause substantial financial and environmental losses when managed separately. As we have demonstrated, it is possible to combine both issues in the way to satisfy both economic and ecological requirements. For that reason, it is necessary to consider implementation of the required technologies on a wide scale to use natural resources in the highest possible proportion, with concurrent advancement of environmental protection.

Literatura – References

1. ANDRUSIKIEWICZ W. *Utilization of wastes from salt production* in: *XVI International Conference "Waste Recycling – Recyklace Odpadu"*, Vysoká Škola Báňská – Technická Univerzita Ostrava 2012: 7–10.
2. ANDRUSIKIEWICZ W., TORA B. *New technological solutions in processes of salt recovery in the brewing process* in: *ICNOP'12, X International conference on Non-ferrous ore processing, KGHM Cuprum Sp.z o.o. CBR*, 2012: 154–164.
3. ANDRUSIKIEWICZ W. "Research of Purification Effect of Saline Mine Water from the Mines KGHM "Polska Miedź" S.A." *Inżynieria Mineralna – Journal of the Polish Mineral Engineering Society* 2/34(2014): 245–250.
4. *Bilans gospodarki surowcami mineralnymi Polski i świata 2013.* Państwowy Instytut Geologiczny – Państwowy Instytut Badawczy, Warszawa 2015.
5. *Bilans zasobów złóż kopalin w Polsce wg stanu na 31.XII.2014 r*. Państwowy Instytut Geologiczny – Państwowy Instytut Badawczy, Warszawa 2015.

Możliwość odzyskiwania odpadów z produkcji soli kamiennej

W artykule poruszono problem zagospodarowania odpadów pochodzących z wydobycia i przeróbki soli kamiennej, a także słonych wód kopalnianych. Omówione zostały sposoby przygotowania solanki na potrzeby dalszej przeróbki. W tym kontekście przedstawiono na podstawie istniejącej instalacji możliwość wspólnego zagospodarowania pyłów solnych i słonych wód dołowych w sposób umożliwiający pozyskanie soli warzonej, będącej towarem handlowym. Omówiono także potencjalne możliwości podobnego zagospodarowania pyłu solnego oraz zasolonych wód dołowych w jednej z kopalń należących do KGHM „Polska Miedź" S.A.

Słowa kluczowe: sól kamienna, odpady solne, solanka, oczyszczanie solanki, ochrona środowiska