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MANAGEMENT OF SALT HYDRATES IN PHOTOVOLTAIC INSTALLATIONS IN LIGHT OF EXISTING ENVIRONMENTAL LEGISLATION

ZARZĄDZANIE HYDRATAMI SOLI WYKORZYSTANYMI W INSTALACJACH FOTOWOLTAICZNYCH W ŚWIETLE OBOWIĄZUJĄCYCH PRZEPISÓW DOTYCZĄCYCH OCHRONY ŚRODOWISKA

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Abstract

This paper discusses an environmental criterion rarely addressed in the literature for the selection of salt hydrates for use in photovoltaic installations as Phase change materials. The aim of the paper is to assess the possibility of utilization of used salt hydrates from photovoltaic installations according to current Polish legal requirements concerning the environment. The properties of the composition components of hydrated salts were discussed in terms of their safety for the environment before and after the period of exploitation in photovoltaic panels. A method of dealing with used salt hydrates was proposed and a waste code was assigned. It has been established that spent salt hydrates will be allowed to be collected in no-outflow tanks and accepted at liquid waste collection points, which operate at water supply and sewerage companies, and the load of permissible pollutants should not exceed the value for industrial sewage.

Keywords: photovoltaic, environmental, PCM, utilization, salt hydrates

Streszczenie

W artykule omówiono rzadko poruszane w literaturze kryterium środowiskowe wyboru hydratów solnych do zastosowania w instalacjach fotowoltaicznych jako materiałów zmiennofazowych (PCM). Celem pracy jest ocena możliwości utylizacji zużytych hydratów soli z instalacji fotowoltaicznych zgodnie z aktualnymi polskimi wymaganiami prawnymi dotyczącymi środowiska. Omówiono właściwości składników kompozycyjnych soli uwodnionych pod kątem ich bezpieczeństwa dla środowiska przed i po okresie eksploatacji w panelach fotowoltaicznych. Zaproponowano sposób postępowania ze zużytymi hydratami solnymi i nadano im kod odpadu. Ustalono, że zużyte hydraty solne będą mogły być gromadzone w zbiornikach bezodpływowych i przyjmowane w punktach gromadzenia nieczystości ciekłych, działających przy przedsiębiorstwach wodociągowo-kanalizacyjnych, a ładunek dopuszczalnych zanieczyszczeń nie powinien przekraczać wartości dla ścieków przemysłowych.

Słowa kluczowe: fotowoltaika, środowisko, PCM, utylizacja, hydraty solne

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1. INTRODUCTION

Solar energy is one of the most promising renewable energy sources because it is free, available in all locations and non-polluting [1]. There are many types of technologies used to produce electricity based on the principle of photovoltaics. The main technology is crystalline silicon used commercially. The efficiency of silicon solar cells is in the range of 18-22% with an upward theoretical limit of 33% [2]. Other technologies are still being explored to produce more efficient solar cells [3]. Of particular interest in the scientific world is the use of salt hydrates as phase change materials (PCM) for thermal energy storage in photovoltaic systems [4-7]. The performance of classical systems depends on: load resistance, sunlight intensity, temperature cell, shading and crystal structure [8]. When the cell temperature rises above its standard operating temperature (25°C), the panel operates less efficiently and efficiency losses can range from 0.3-0.4% per degree [8]. It is possible to improve the efficiency of the panels by using specially dedicated storage with low-temperature phase-change material in PV modules. For this purpose, hydrated salts are placed in carbon nanotubes, for example [9]. The PV module generates heat through dedicated storage, thus it is possible to convert more of the stored heat into electricity using the Seebeck effect [10].

Salt hydrates, which make up a large portion of inorganic *PCM,* have a number of beneficial properties that predispose them to applications in solar heating systems [4, 11]. These include: low price, large-scale availability non-toxicity, good compatibility with materials thermoplastic, high latent heat of phase change per unit volume, high thermal conductivity, low volume change with dehydration and thermal hydration [11-15]. For photovoltaic panel systems, salt hydrates are used with well-defined phase transition temperature ranges that must meet practical applications. If these cannot be met, the salt hydrates can be mixed to adjust their melting point (MLT). The most common salt hydrates used in photovoltaic installations are sodium sulfate decahydrate (MLT = 32.4°C) [16], calcium chloride hexahydrate (MLT = 24°C; 30°C) [17] and magnesium chloride hexahydrate (MLT = 58°C) [16]. The most commonly cited problems with the use of salt hydrates include: incongruent and semi-congruent melting resulting in irreversible dehydration and loss of efficiency and difficulty in crystal nucleation, overcooling and corrosive properties [15]. These properties can be continuously improved, e.g. by combining *PCM* with porous materials the problems of phase separation and leakage during phase transformation are solved. The use of nanoparticle additives improves the thermal conductivity and reduces the subcooling of most hydrates [18].

On the one hand, salt hydrates are considered to be non-toxic substances [15] on the other hand, it seems obvious that the toxicity of a substance is determined by its dose [19]. It is also an indisputable fact that after use, salt hydrates will constitute waste that requires disposal. In literature, the authors [19, 20] indicate that environmental safety is one of the most important criteria for selecting hydrates salts. Donkers et al. [19] emphasize that the safety assessment of hydrates should be evaluated on a case-by-case basis. The authors write that there are salt hydrates that are clearly listed as toxic in the *Material Safety Data Sheets (MSDS)* [19, 20]. In addition, some of them can react to form by-products such as acids HCl, H_2S [20] whether oxidizing substances ($Ca(ClO_4)_2$), $CrCl_2$ and $FeCl_2$ [19, 20]. In addition, the authors [9, 19] indicate that for all hydrates, the stability of the material should be considered in terms of service life. This is because it cannot be ruled out that the properties of salt hydrates and their reaction with the material will not change after years of use. Zbair and Bennici [20] write that most salts are compatible for long-term exposure with stainless steel. However, contact of some salt hydrates with carbon steel and aluminum can lead to modification of the carrier material.

In spite of the fact that salt hydrates are still one of the top topics in the field of renewable energy sources, only in a publications authors pay attention to the importance of the environmental criterion of their selection [19, 20]. There is a lack of information in the literature regarding guidelines for handling hydrates at the selection stage and before and after their operational life. The authors also did not reach a paper that evaluated the disposal options for spent hydrated salts. This seems to be a key element of the environmental criterion, especially in countries where environmental policy is very restrictive. The problem is also becoming relevant in Poland, where fossil fuels are being abandoned and renewable energy sources are gaining in importance.

In view of the above, the authors analyse in the publication how to deal with salt hydrates from photovoltaic installations in accordance with Polish environmental legislation at the stage of their selection, before and after operation. Then they present the concept of disposal of used salt hydrates.

2. ENVIRONMENTAL CRITERION FOR SELECTION OF HYDRATED SALTS

One of the most important criteria for the selection of hydrated salts as *Thermochemical Storage Materials (TCMs)* in PV plants is the evaluation of their environmental safety. The selection of suitable substances should take into account their properties both before and after the operation period. Hydrated salt compositions should be selected in such a way that they do not constitute hazardous waste after use and have as many characteristics as possible of inert waste in the meaning of the Act on Waste [21]. It is important that these substances have a stable chemical composition, do not undergo biodegradation processes, do not adversely affect the matter they come into contact with, do not pollute the environment and the negative impact of the leachate on the environment is insignificant, do not pose a threat to the quality of surface water, groundwater, soil and ground. In case of mixtures of substances, all environmentally hazardous properties should be assessed using the concentration limits of the components of the mixture classified as environmentally hazardous substances [22]. The characteristics of a substance can be assessed on the basis of Safety Data Sheets, which are the basic document defining the properties of a chemical and its scope is determined by the European Parliament Regulation No. 1907/2006 on the Registration, Evaluation, Authorization and Restriction of Chemical Sales. According to the regulation 1907/2006/WE The Safety Data Sheet of a chemical substance is the main tool for the flow of information on hazards and risk management in the marketing of these substances. On its basis we can assess: what environmental legislation the substance is subject to, procedures in case of accidental release into the environment, handling and storage of the substance, chemical stability, reactivity and possibility of hazardous reactions, hazardous properties of salts, toxicity of the substance for organisms including bioaccumulation and susceptibility to degradation in the aquatic environment, mobility in soil, waste management.

3. DEALING WITH SALT HYDRATES USED IN PHOTOVOLTAIC INSTALLATIONS BEFORE AND AFTER THEIR EXPLOITATION IN THE LIGHT OF LEGAL ACTS

3.1. Before the period of operation

In addition to the selection of environmentally safe components of hydrated salts according to the criteria discussed in section 2, the appropriate way of handling such substances when designing photovoltaic installations is important. Investors should make sure that the designed installation will not be included in the Regulation of the Minister of Environment of 27 August 2014 on types of installations that may cause significant pollution of particular natural elements or the environment as a whole [23]. Next, they should set waste prevention as a goal. According to the Waste Act: *means the measures taken in respect of a product, material or substance, before it becomes waste, that reduce (a) the quantity of waste, including through reuse or prolongation of the continued use of the product, (b) the negative environmental and human health impacts of the waste generated, (c) the content of harmful substances in the product and material.* Therefore, at each stage of plant design, environmental aspects should be taken into account with the intention of improving the characteristics of the impact that a given product has on the environment throughout its entire life cycle, the so-called 'eco-design'. The realization of this goal could be introduced by selecting as components of the salt composition hydrated substances that do not have a negative impact on the environment and have as many characteristics of inert waste in the meaning of the Act on Waste [21] and by constant control of changes in the properties of hydrated salt compositions supported by laboratory tests.

Particular attention should be paid to the fact that the hydrated salt compositions and their degradation products do not pose chronic or delayed potential hazard for the aquatic environment in accordance with the Regulation of the Minister of Health of 10 August 2012 on the criteria and method of classification of chemical substances and their mixtures. Hydrated salt compositions created should be susceptible to rapid degradation in the aquatic environment (when the ratio of BOD_5 *(Biochemical oxygen demand)*/*COD(Chemical oxygen demand)* is $\geq 0{,}5$), should not bioaccumulate ($\log P < 1$ – n-octanol-water partition coefficient for organic matter) and shall not be toxic to fish or Daphnia on a chronic basis at a concentration 1 mg/dm^3, at prolonged exposure > 1 mg/dm^3. It is useful to create salt compositions from inorganic substances, which in turn can be transformed by normal environmental processes to either increase or decrease the bioavailability of toxic species. Additionally, substances should not be placed on the list of Substances of Very High Concern (*SVHCs*) [30]. Substances fulfilling one or more of the criteria defined in Article 57 of the *REACH* standards for the Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (*REACH*) can be identified as *SVHC*. Substances on *REACH SVHC* list are substances meeting the criteria for classification as carcinogenic, mutagenic or reprotoxic (*CMR*) category 1 or 2; persistent, bio-accumulative and toxic (*PBT*) substances; or very persistent and very bio-accumulative (*vPvB*) substances; substances for which there is evidence for similar concern, such as endocrine disruptors.

Another important criterion is that the hydrated salt compositions created should not interact with the material they contact. The *TCM* material should have a specified lifetime of 15-20 years, during which the applied substance must retain its properties, and the rate of its decomposition should be as long as possible [4]. Undesirable reactions include: susceptibility to oxidation in humid environments ($CrCl_2$, $FeCl_2$) (risk of explosion during fire); decomposition of substance by degassing ($MgCl_2$) separated HCl at high temperatures (*TCM* weight reduction, possible corrosion and increase in pressure); (Na_2S) with the release of highly corrosive H_2S [11].

The following is a summary of environmental requirements that should guide investors in the selection of components of salt hydrate compositions for photovoltaic installations:

– should not be classified as hazardous substances "N" in the Regulation of the Minister of Health of 10 August 2012 [29] on the criteria and classification of chemical substances and their mixtures.
– Substances should not be placed on the list of Substances of Very High Concern (*SVHCs*).
– Published by *ECHA* and updated every six month [30].
– Substances should not have hazardous properties (substance after use should not meet the definition of hazardous waste according to the Law on Waste [21], moreover they should not be classified in the *MSDS* as explosive, reactive under normal environmental conditions.
– The substance should be presented in the safety data sheet as chemically stable under normal environmental conditions.
– Substance in the safety data sheet should be classified as not hazardous to the aquatic environment $LC_{50} > 100$ mg/l (The value of LC_{50} for a substance is the concentration required to kill half the members of a tested population after a specified test duration) according to 1272/2008/EC, substance is not bioaccumulative $logP < 1$, substance should be susceptible to degradation in the aquatic environment $BOD_5/COD \geq 0.5$.

3.2. After the operation period

Spent salts hydrated after a period of operation will meet the definition of waste under the Waste Act [21]. Waste according to Art. 3 is defined as "substance that the holder disposes of or intends or is obliged to dispose of". It should not contain substances particularly harmful to the aquatic environment, causing water pollution that should be eliminated (List I), and substances particularly harmful to the aquatic environment, causing water pollution that should be reduced (List II). The cited lists are included in the Regulation of the Minister of Maritime Economy and Inland Navigation of 12 July 2019 [27] on substances particularly harmful to the aquatic environment and conditions to be met when discharging waste water into waters or onto the ground, and when discharging rainwater or snowmelt into waters or into water facilities. Used salt compositions should not constitute hazardous waste within the meaning of Commission Regulation (EU) No 1357/2014 of 18 December 2014 [28]. As hydrated salt compositions are often mixtures of substances and their effects in duet are not always known it is worthwhile to perform additional laboratory analyses such as: stability of the chemical composition and thermal stability in order to exclude unfavorable reactions and to assess the impact on the lifetime of the installation, evaluation of pH and specific electrical conductivity in the converter operating temperature range in order to assess possible concentration of the substance under certain pH conditions and unfavorable corrosive effects or substance leaks, evaluation of particle size changes to exclude dehydration, determination of organic matter content and analysis of possible transformations, determination of inorganic carbon content (as a background for testing to exclude release of carbon compounds from the casing to the hydrated salts under operating conditions of the converter), evaluation of the effects of salt compositions on plant growth (new knowledge regarding assessment of the impact on the environment and in the direction of searching for potential methods of disposal).

The following is a summary of the requirements that hydrated salt compositions should meet when they become waste so that they do not have a potentially harmful effect on the environment or on the carrier:

- pH (6.5-9);
- chlorides < 1000 mg/l, sulfates < 500 mg SO_4/l, sodium < 800 mg/l, potassium < 80 mg/l;
- salt compositions are thermally stable at temperatures in the range of 0-70°C;
- salt compositions have a stable chemical composition, which will not change the classification of the chemical substance (permissible deviations are given in Table 1). The table is derived from the Regulation of the Minister of Health of 10 August 2012 on the criteria and classification method of chemical substances and their mixtures;
- hydrated salt compositions should not show any carrier material in their composition;
- hydrated salt compositions should not show significant compositional changes particle size under converter operating conditions. According to ISO 13320:2009, the precision should be less than 3% for grains D_{v50} and less than 5% for grains D_{v10} i D_{v90}.

Table 1. Permissible deviations from the initial component of the substance depending on concentration of the initial component in the mixture

Range of starting concentrations of the component in the mixture	Permissible deviation from initial component concentration
concentration < 2.5%	±30%
2.5% < concentration < 10%	±20%
10% < concentration < 25%	±10%
25% < concentration < 100%	±5%

4. WASTE CODING AND TREATMENT

According to the Regulation of the Minister of Environment of 9 December 2014 on the catalog of waste [24]. The entity generating waste is obliged to assign a waste code. In turn, according to the Act of 14 December 2012 on waste [21]. The waste should be handed over to an entrepreneur, who has a permit from the competent authority for waste management or the method of waste disposal should be agreed with the competent local Department of Environmental Protection. The authors proposed a waste code for the used hydrated salt compositions from photovoltaic installations according to Table 2. At present, the Waste Law [21] art. 122 prohibits landfilling 1) occurring in liquid form, including waste containing water in an amount exceeding 95% of the total mass, excluding sludges. Therefore, the waste generated cannot be disposed of in liquid waste dumpsters. The waste with the assumed waste code 161002 can be collected in non-drainage tanks and accepted at the liquid waste disposal points, which operate at the water and sewerage companies.

Table 2. Proposed waste codes for used hydrated salts from photovoltaic installations

1610	Hydrated liquid wastes for off-site recovery or disposal
161001*	Hydrated liquid wastes containing hazardous wastes
161002	Hydrated liquid wastes other than those mentioned in 161001

Municipalities are managed in this respect under the Act of 13 September 1996 on Maintaining Cleanliness and Order in Municipalities [25]. In accordance with the Regulation of the Minister of Infrastructure of 17 October 2002 on the conditions for introduction of liquid waste to septic tanks [26], the permissible load of pollutants in liquid sewage, which is discharged to a sewage lifting station, is agreed between the owner of the sewage lifting station and the owner of the sewage treatment plant where the sewage will be treated and results from the balance of quantity and quality of sewage and the treatment processes applied in the sewage treatment plant. Therefore, it is not possible to give specific pollution loads that hydrated salt compositions should meet in order to be accepted at such a station. However, it is advisable that the compositions meet the more restrictive standards that are given for industrial wastewater. Within the meaning of the Water Law and Environmental Protection Law, waste water, when introduced to water or to the ground becomes sewage. According to the Regulation of the Minister of Maritime Economy and Inland Navigation of 12 July 2019 [27] on substances particularly harmful to the following daily average limits for expected pollutants are given for the water environment and the conditions to be met when discharging waste water into waters or onto the ground, as well as when discharging rainwater or snowmelt into waters or into water facilities: temperature < 35°C, pH 6.5-9, chlorides 1000 mg/l, sulphates 500 mg SO_4/l, sodium 800 mg/l, potassium 80 mg/l.

5. CONCLUSIONS

In this publication, the authors discuss which properties of chemical substances, that are components of compositions of hydrated salts in photovoltaic installations, should be taken into account to make them safe for the environment. Properties for the substance before and after the period of operation are presented. The directions of proceeding with salt hydrates at each stage of designing photovoltaic installations were discussed. A method of dealing with used salt hydrates was proposed and a waste code was assigned. It has been established that spent salt hydrates (waste code 161002) will be allowed to be collected in no-outflow tanks and accepted at liquid waste collection points, which operate at water supply and sewerage companies. The load of permitted pollutants should not exceed the values for industrial wastewater in accordance with the Ordinance of the Minister of Maritime Affairs and Inland Navigation of 12 July 2019 on substances that are particularly harmful to the aquatic environment and the conditions to be met when introducing wastewater into waters or into the ground, and when discharging rainwater or snowmelt into waters or into water facilities.

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