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Assessment of the Main Threats to Injection Well Damage Caused by Reservoir Waters using AquaChem Software as well as Laboratory Tests Application

Introduction

One of the most effective methods of managing generated water and other liquid wastes is their injection into an absorptive horizon. The process of brine separation from excavated hydrocarbons, pollution of generated water with the aid of chemicals, and contact with the air causes serious alternations in reservoir waters properties. Taking this into account, it is necessary to receive a licence for reservoir water injection [6, 9, 10].

As research results show, reservoir water (brine) coming from nearby gas and oil wells, make up most of the water injected into the reservoir. The chemical content depends on collector properties and is similar in the case of all water samples tested, but the concentrations of individual chemical compounds vary in a wide range [1].

Injecting reservoir water to absorptive horizons is undoubtedly ecologically beneficial because it means waste-free elimination of harmful substances from an active biosphere. Moreover, it provides significant cost reduction connected with the technical infrastructure usage possibilities. However, this kind of reservoir water and sewage management fulfills the requirements determining underground waste storage. Apart from this, monitoring and modification of injected water parameters are necessary in order to protect boreholes from injection zone damage [8]. It results in the optimum usage of the absorptive horizon storage capacity.

The main aim of the injection installation is to eliminate reservoir water, which was obtained during hydrocarbon and liquid sewage generation by the oil and gas mining industry from the active biosphere. They must be stored safely in an exploited reservoir [7]. Taking this into con-

sideration, the aim of the treatment process is not total elimination of pollutants, but the modification of injected water properties, which would prevent plugging of the injection zone and enable maximum elongation of reliable work of the absorptive well.

The near-wellbore zone of the absorptive horizon is the most essential site, in which the most important phenomena influencing the work of the injection well takes place [8]. Among the processes there are:

- blocking of the near-wellbore zone caused by insufficient filtration of injected water from sediments and suspensions,
- precipitation of reaction products between introduced water and absorptive layer,
- sediment precipitation of metal oxides as corrosion products of injection well pipes,
- formation of emulsion in the near-wellbore zone,
- separation of gases introduced with injected water,
- microorganisms growth and negative phenomena caused by their living processes.

Research results show that the main factors causing damage of the injection well are sediments and suspensions consisting of rocks (silt, rock particles, sand, dusts, colloidal silica etc.). Suspensions included in water, which was not completely filtered, can create sediments (filtration cake) directly on the most damage-susceptible wall surface of the absorptive horizon [4, 11]. Suspensions, which are smaller than the size of a rock collector pore, can also move into deeper layers of the bed. Through gravitational sedimentation or adsorption on pore walls, they can limit permeability of the rock collector [2].

Materials and methods

Samples of reservoir water (brine), destined for injection into the absorptive well, were used in research. In order to determine characteristics of the cluttered waters, physical-chemical analyses were done according to obligatory procedures. The analyses of contents were as follows: contents of chlorides (a titration method), bicarbonates, sulphates, calcium, magnesium, potassium, iron (analyses done with ISIS 9000 Spectrometer using reagents and dish tests by DrLange and Merck). Content of sodium, pH reaction and electrochemical potential (Eh) of the water samples were determined with the multiparameter instrument WTW i-330 and electrode measurements based on calibrated standard solutions.

Analytical accuracy estimated by standard deviation is below 0.01% and 0.1% for analyses done with a spectrometer and measurement electrodes respectively.

Obtained analytical data served as material for calculations done with the AquaChem software and the following indexes: Langelier Saturation Index (LSI), Ryznar Stability Index (RSI), Larson-Skold Index which enabled determination of precipitation possibilities and stability of carbonate deposits as well as corrosive characteristics of water.

Saturation pH – describes a pH reaction value in an equilibrium point for a given concentration of carbonates. Growth or decrease in pH value may cause sediment precipitation or dissolution respectively.

Langelier Saturation Index (LSI) – a model based on a definition of saturation, used as an index of water saturation with CaCO_3 . LSI can be interpreted as a change of water reaction to obtain equilibrium. When the water is in a borderline range ($-0.5 < \text{LSI} < +0.5$), even small changes in parameters (composition, temperature, evaporation) cause precipitation of solids.

When the value is over 2.0, there is acceleration in sedimentation of huge amounts of wastes.

Ryznar Stability Index (RSI) – a model based on a definition of saturation, it enables the estimation of dependence

between CaCO_3 saturation point and sediment precipitation. Optimum values are 6.0÷7.0. When the RSI value is below 5.0, there is acceleration in sediment precipitation whereas when it is over 7.0, increase in corrosivity of water (uniform corrosion) takes place.

Larson-Skold Index – describes water corrosivity in relation to mild steel (based on data of water pipe corrosion). Larson-Skold Index value below 0.8 is optimal (no corrosion), whereas its increase over 1.2 suggests the possibility of pitting corrosion.

AquaChem simulation data suggest only general directions of the process and they are not used for quantity counting. In this case statistical errors were not estimated.

In laboratory tests, collective water (Sample 4) designed for injection was used. The sample contained the following amounts [mg/dm^3] of basic components: $\text{Cl}^- = 54171$, $\text{HCO}_3^- = 173$, $\text{Na}^+ = 30241$, $\text{Ca}^{2+} = 3104$, $\text{Mg}^{2+} = 758$. The pH value was 6.12 whereas electrochemical potential (Eh) equalled 165 mV.

A part of the water sample was aerated (to Eh = +200) [5], coagulated and filtered in order to create conditions close to natural and compare the influence of actions taken to prepare water for injection, on brine corrosivity. In the research the influence of brine treatment (pH value correction and $\text{Al}_2(\text{SO}_4)_3$ coagulation) and the influence of corrosion inhibitor dosage quantity on the injection process were taken into account. In addition, research on water corrosion with an alternative coagulant PAX-16 (polyaluminium chloride) was done. Plates used in the test were made of N80 steel.

A coupon test of water corrosion after aeration and without aerating (crude water) after filtration of sediments and suspensions from water samples (comparative samples) was also done.

The corrosion tests were done at a temperature of 25°C comparable to the temperature the lower part of the injection well.

Determining injected water properties using AquaChem as well as laboratory research

Determinating the origin of waste and their quantities can serve as proof that the majority of injected water is brine excavated from nearby gas plants – whereas less frequently – water coming from oil wells. All these water types have almost a similar set of basic compounds, and differences are caused only by alternations in their concentrations in a wide range, which is presented in the Schoeller Plot below (Fig. 1).

(Fig. 2) presents radial diagrams of alternations in the concentration of basic compounds in selected brine samples injected into the wellbore. As analytical data show, alternations in the concentration of basic compounds are explicit, however, they do not influence the general properties of the injected water. Chemical properties are connected with the ability of sediment precipitation in a wellbore and mixing of subsequent parts of brine.

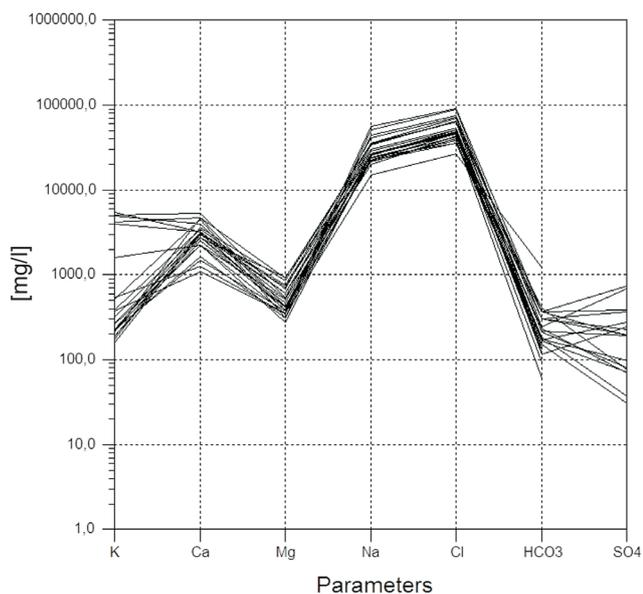


Fig. 1. Schoeller Plot – alternations in the concentration of basic compounds of brine samples injected into an adsorptive borehole

Calculations, done with the use of AquaChem ver. 5.1 software, showed that all tested samples of injected waters are in a narrow range of chemical equilibrium, which can be moved into a direction of dissolution or sediments carbonate precipitation through insignificant alternations in the chemical properties (Tab. 1).

During preparation of water for injection after aeration which causes the precipitation of metal ions (Fe, Mn) turning into solid oxides and the removal of sediments and suspensions, it is vital to obtain water of pH close to the pH of previously injected water (stabilisation of reaction at a level of $6 < \text{pH} < 7$). The pH correction could be done applying appropriate chemicals in doses. An increase in water alkalinity is particularly dangerous because it causes carbonate sediment precipitation.

The next crucial group of substances, which can threaten the reliability of the injection well, are ions of metals, particularly iron and manganese ions. These metals which are, present in reduced forms in reservoir water, can create

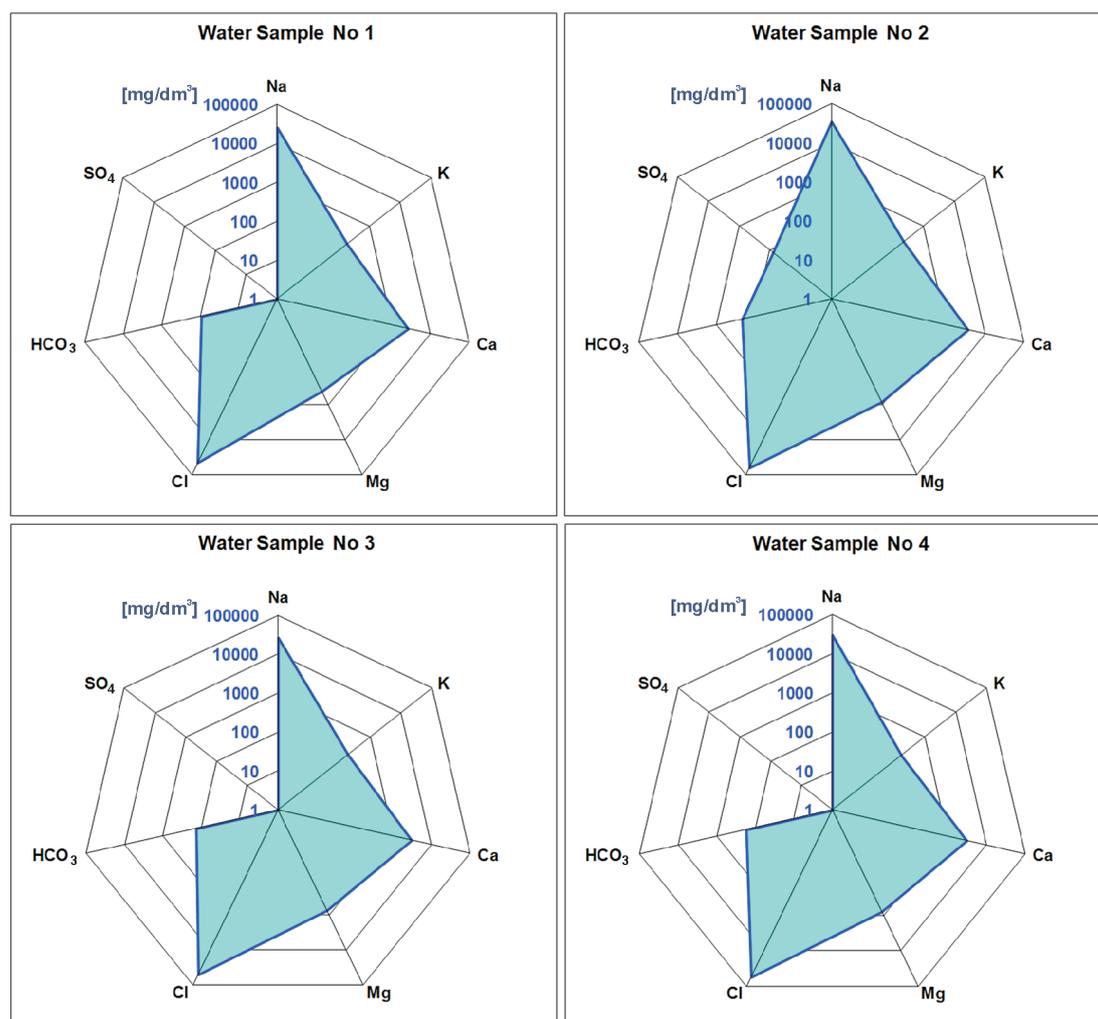


Fig. 2. Radial diagrams of basic compounds concentrations in consecutive parts of reservoir water injected into absorptive well

Tab. 1. Indexes values describing carbonate sediment precipitation and anticipated corrosion properties for subsequent parts of injected water (estimated using AquaChem software)

| Water sample | Saturation pH | LSI | RSI | Larson-Skold Index | Description |
|--------------|---------------|------|------|--------------------|--|
| No 1 | 6.09 | 0.18 | 5.91 | 829.95 | Borderline scale potential. Changes in water quality, temperature or evaporation can move equilibrium to CaCO ₃ precipitation or dissolution area. Corrosion index increased. |
| No 2 | 5.59 | 0.52 | 5.06 | 515.38 | Scale can form and CaCO ₃ may occur. Low tendency to scale precipitation. Corrosion index increased. |
| No 3 | 5.84 | 0.80 | 5.05 | 598.37 | Scale can form and CaCO ₃ may occur. Low tendency to scale precipitation. Corrosion index increased. |
| No 4 | 5.74 | 0.38 | 5.36 | 538.44 | Scale can form and CaCO ₃ may occur. Low tendency to scale precipitation. Corrosion index increased. |

suspensions and colloidal solutions as a result of alternations in physical and chemical parameters. Alternatively, as ions they can participate in complicated processes occurring in a reservoir.

According to simulations done with the AquaChem software, it was observed that injected brine had increased corrosion properties – Larson-Skold Index (Tab. 1). Taking this into consideration, there is a threat of damage in the near-wellbore zone. It may be caused by corrosion products of the installation and injection well fittings. The corrosion products, forming after filtration of sediments, cannot be removed from the injected water, and thus perreating directly into the near-wellbore zone can quickly damage it.

In order to determine the predicted danger caused by corrosive properties of injected waters, tests defining corrosion speed were done.

According to the obtained data, injected water has

a high level of corrosion aggressiveness (Tab. 2.) in relation to the construction material of pipings and well fittings. The corrosion speed in the case of water after aeration is about 530 g/m²/year.

Addition of a coagulant, to both aluminium sulphate (after correction of water reaction) and PAX-16 (without pH correction), results in corrosion speed decrease to a level of about 430-440 g/m²/year.

In the case of coagulation with Al₂(SO₄)₃, an increase in dosage of a corrosion inhibitor (used at present during brine treatment), causes gradual decrease in corrosion of injected water to 250 g/m²/year when the optimum dose is 0.5 cm³/dm³ (Fig. 3).

In the case of coagulation with PAX-16, a minimum dose of an inhibitor (0.1 cm³/dm³ of water) results in water corrosion increase, and then a further increase in the dose enables a reduction in corrosion speed to about 210 g/m²/year when the maximum tested dose is 1 cm³/dm³ (Fig. 3).

Tab. 2. Steel N80 plate mass decrease during corrosivity test of water injected with coagulants and corrosion inhibitor

| Test sample No | Corrosion inhibitor dosage [cm ³ /dm ³] | Mass decrease [g/m ² /year] | Test sample No | Corrosion inhibitor dosage [cm ³ /dm ³] | Mass decrease [g/m ² /year] |
|---|--|--|--|--|--|
| coagulation with Al ₂ (SO ₄) ₃ , pH correction and filtration | | | coagulation with PAX-16 and filtration | | |
| 1 | 0.0 | 429.0 ± 40.3 | 6 | 0.0 | 443.5 ± 41.7 |
| 2 | 0.1 | 391.8 ± 35.8 | 7 | 0.1 | 509.1 ± 50.6 |
| 3 | 0.3 | 284.9 ± 23.6 | 8 | 0.3 | 443.4 ± 41.7 |
| 4 | 0.5 | 251.9 ± 20.1 | 9 | 0.5 | 316.6 ± 27.5 |
| 5 | 1.0 | 254.5 ± 20.3 | 10 | 1.0 | 213.1 ± 18.4 |
| control samples | | | | | |
| brine after aeration and filtration | | | not aerated brine after filtration | | |
| 11 | 0 | 529.7 ± 52.6 | 12 | 0 | 324.7 ± 28.2 |

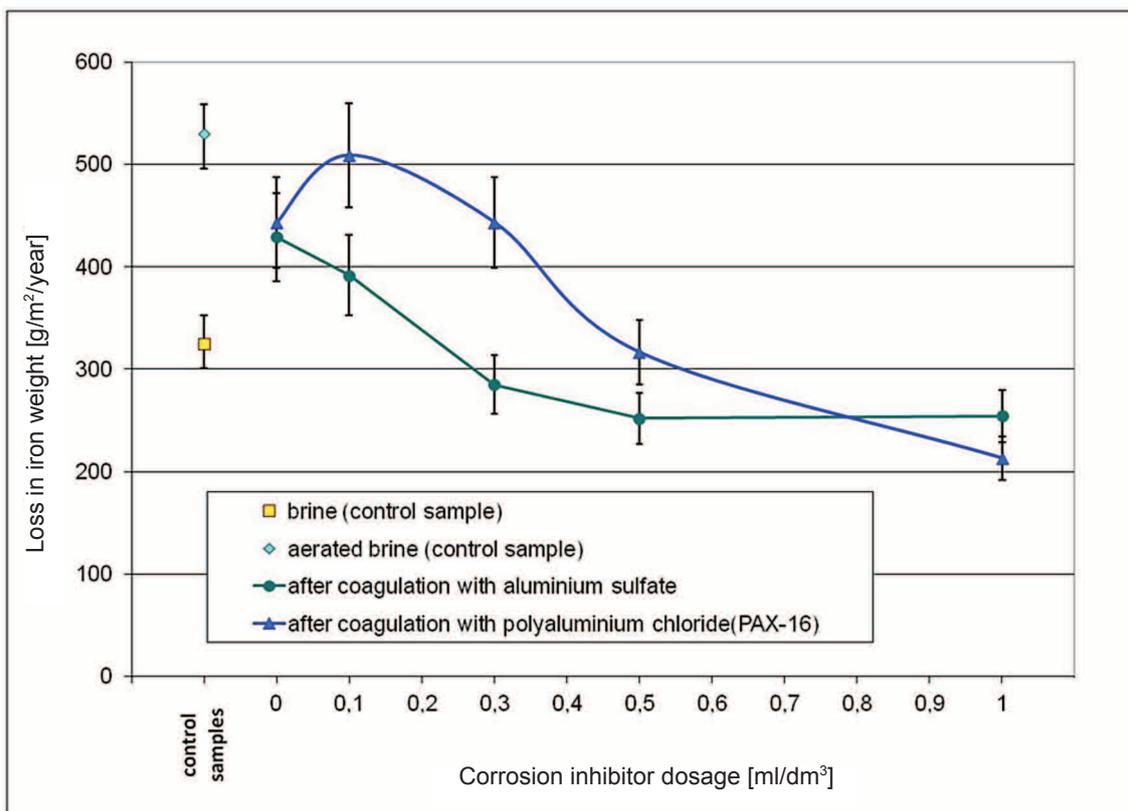


Fig. 3. Corrosivity tests of water prepared for injection after coagulation with aluminium sulphate and polyaluminium chloride (PAX-16) depending on corrosion inhibitor dose

Such high corrosion speed is a grave danger to the reliability of an injection well. Samples of brine after coagulation with $\text{Al}_2(\text{SO}_4)_3$, done applying a different dose of a corrosion inhibitor, as well as a control sample (No. 11) have been presented in the picture below (Fig. 4).

The amount of iron oxides (calculated by using the obtained laboratory data), formed as a result of piping and wellbore fittings corrosion, is about 105 kg/year, which can lead to near-wellbore zone damage in a short period of time.

This serious threat demands doing research on a selection of a more effective corrosion inhibitors and, ultimately the application of other methods to protect wellbore fittings from corrosion [3] (e.g. removal of oxygen from water before injection – corrosion strength of un-aerated brine is only slightly higher than that of aerated brine with an optimum inhibitor dose).

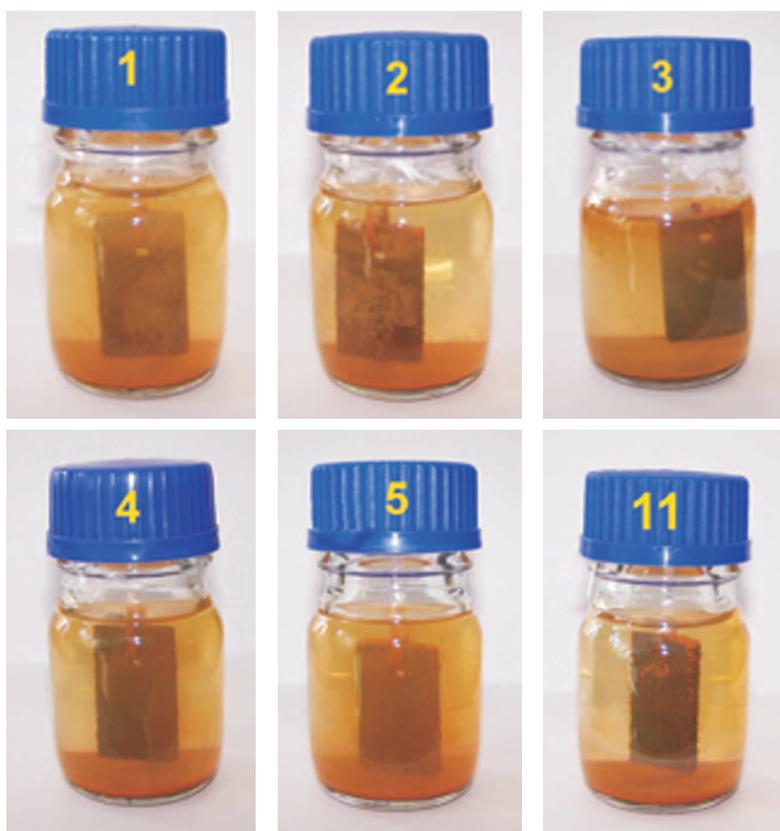


Fig. 4. Brine samples during corrosion test (with $\text{Al}_2(\text{SO}_4)_3$ and corrosion inhibitor) and control sample (No. 11) – brine after coagulation and filtration

Summary

The analyses of the research material allowed us to conclude that, the majority of reservoir waters injected to the absorptive horizon are compatible (they come from reservoirs of a similar geological structure). They should not cause accelerated damage of the near-wellbore zone if they are correctly prepared for injection, which means oxidation of iron ions and the separation of postcoagulant sediments.

The application of the AquaChem software enables determination of the influence of alternations in the main chemical and physical parameters of brines on sediment precipitation and dissolution as well as alternations in corrosion. Owing to this fact, it is possible (with some limits) to predict a safe range of these parameters and to adjust them through appropriate modifications of the water content and other operations, which would prevent near-wellbore zone damage. Calculations and simulations, obtained using AquaChem, can be useful during research on the influence of injected water with diverse contents on

processes taking place during water mixing and contact with reservoir minerals.

The research showed that the main factors threatening the reliability of a borehole are: not completely removed sediments, easily oxidized metal ions (iron and manganese) and – above all – corrosive properties of injected waters, which can cause the formation of iron oxide sediments. Corrosion caused by water injected in contact with wellbore fittings is particularly dangerous. In this phase of the injection process, protection of the near-wellbore zone against iron oxide sediment particles is very difficult.

The removal of sediments would result in huge difficulties and high costs. Stimulation treatment (acidizing) would be necessary if there was an excessive decrease in both permeability of the near-wellbore zone and effectiveness of the injection. Therefore, it is essential to take steps to improve the effectiveness of corrosion inhibition as well as other actions preventing well fittings corrosion.

References

- [1] Jakubowicz P.: *Badania kompatybilności wód zatłaczanych z wykorzystaniem programu AquaChem*. „Nafta-Gaz” 2010, nr 5 s. 383–389.
- [2] Liu X., Civan F.: *Formation Damage and Skin Factors Due to Filter Cake Formation and Fines Migration in the Near-Wellbore Region*. SPE 27364 paper, Proceedings of the 1994 SPE Formation Damage Control Symposium, pp. 259–274, Lafayette, Louisiana, Feb. 9–10, 1994.
- [3] McCafferty E.: *Introduction to Corrosion Science*. Springer, 2010.
- [4] Pang S., Sharma, M.M.: *A Model for Predicting Injectivity Decline in Water Injection Wells*. SPE Formation Evaluation, pp. 194–201, September, 1997.
- [5] Pourbaix M.: *Atlas of Electrochemical Equilibria in Aqueous Solutions*. Pergamon, New York 1966.
- [6] Rychlicki S., Stopa J., Solecki T.: *Składowanie odpadów w górotworze z wykorzystaniem otworów wiertniczych*. „Gaz, Woda i Technika Sanitarna” 2001, nr 10.
- [7] Solecki T.: *Badania procesu włączania wody odwiertami w porowate warstwy chłonne*. Praca doktorska, AGH, Kraków 1981.
- [8] Solecki T.: *Wybrane problemy stosowania odwiertów chłonnych w aspekcie ochrony środowiska przyrodniczego*. Materiały Konferencji Naukowo-Technicznej pt.: Ochrona środowiska w górnictwie naftowym, Jasło 1988.
- [9] Ustawa z dnia 27 kwietnia 2001 r. o odpadach (tekst jednolity Dz.U. 2007 Nr 39, poz. 251) z późniejszymi zmianami.
- [10] Ustawa z dnia 9 czerwca 2011 r. Prawo geologiczne i górnicze (Dz.U. z 2011 nr 163, poz. 981).
- [11] van Oort E., van Velzen J.G.G., Leerlooijer K.: *Impairment by Suspended Solids Invasion: Testing and Prediction*. SPE Production & Facilities, pp. 178-184, August 1993.



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