Possible Uses of Synthetic Gypsum in Salt-Cavern Filling

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Abstract

Large quantities of synthetic gypsum are obtained from the wet flue-gas treatment process during coal burning. Synthetic gypsum is a full-value by-product that can be processed in various industries. However, overproduction causes that considerable quantities of synthetic gypsum are rather stockpiled on surface storage dumps. This paper presents an optional use of synthetic gypsum to prepare mixes based on fully saturated brine designed for salt-cavern filling. Such an operation allows, on the one hand, to recover full-value brine collected in a cavern, and, on the other hand, to reduce the quantities of gypsum dumped on land surface. In addition, filling of salt caverns with gypsum mixes is geomechanically more beneficial than cavern filling with brine. That method is also important for environmental protection reasons.

Keywords: salt caverns, synthetic gypsum, liquidation of caverns, environmental protection

Introduction

Each type of solid-mineral mining causes intervention in the natural environment and geological one in particular. Apparently, the least invasive seems to be the solution mining method applied in rock salt. Only well heads and pipelines are placed on the surface to leach a cavern several hundred metres underground. Cavern volumes may reach millions of cubic metres. To maintain cavern stability, the cavern has to be filled with a medium, usually saturated brine. In the case of underground storage facilities, caverns are filled with petroleum products or natural gas. However, salt-cavern operation for storage purposes is limited in time. At some point of time, such an operation has to be terminated. Cavern liquidation consists in filling of the caverns with saturated brine, which is a full-value raw material suitable for use in chemical plants. Consequently, losses are estimated at ca. 15% of the depleted cavern volume.

Consequently, it is fully justified to seek the solutions which will, on the one hand, extract brine from caverns and, on the other hand, ensure long-term cavern stability. Most certainly, such objectives are met by classical hydraulic filling processes based on sand. However, that solution is costly owing to economic issues. The cavern filling material we seek should fulfil all the safety requirements understood as geological environment safety, including cavern stability after a period of mining or underground storage operation. Of course, those are not the only characteristics specified for the material. We should also take into account material availability, price etc. With so defined assumptions, our attention was turned to a possible use of certain mixes, with addition of synthetic gypsum, in the process of salt-cavern filling.

Synthetic Gypsum

Synthetic gypsum, or desulfogypsum, is often described as IOS. It is a by-product of scrubbing smokestacks in flue-gas desulphurization installations. Also, 'REA-Gips' is a generally used international term (the abbreviation comes from the German name of REA desulphurization installations: Rauchgasentschwefelunganlage). Synthetic gypsum is produced in the process of wet desulphurization of the flue gas generated in power and cogeneration plants burning hard or brown coals. IOS gypsum is characterized by low natural radiation and low heavy metal and other contamination contents, as well as high chemical purity (Jarema-Suchorowska 2013).

Synthetic gypsum is produced in four basic stages:

Stage 1: desulphurization. The flue gas generated as a result of burning hard or brown coals in boilers is treated in electrostatic precipitators (electrofilters) to remove fly ashes and pumped into suspension containing lime dust. Thus, calcium sulphate hemihydrate is produced:

$$SO_2 + CaCO_3 + ½\,H_2O \longrightarrow CaSO_3 \cdot ½\,H_2O + CO_2$$

The above reaction generates sulphite slurry which intercepts sulphur compounds. However, further operations are required to obtain the form of gypsum.

Stage 2: oxidation. During that process, which takes place in the air stream, gypsum is crystallized:

$$2\,CaSO_3 \cdot ½\,H_2O + 3\,H_2O + O_2 \longrightarrow 2\,CaSO_3 \cdot 2\,H_2O$$

Stage 3: segregation. That process is intended to dehydrate gypsum slurry and separate impurities. The process is mechanical and conducted in a hydrocyclone.

Stage 4: washing. The mix obtained in the previous stage is subjected to washing out chloride, sodium, and magnesium. Finally, after draining, proper synthetic gypsum is obtained.

REA-gips produced by that process is a small-grain material whose grains belong mostly to the size range of 50-150 μm. The aggregate density of gypsum amounts to ca. 2.35 Mg/m^3, and bulk density is from 0.6 to 1.25 Mg/m^3. Gypsum humidity is contained in the range from 7 to 10%. Calcium sulphate dehydrate is the main component of synthetic gypsum, constituting 95% of gypsum weight. The remaining components include calcium and magnesium carbonates, iron oxides, silicon dioxide, trace quantities of heavy metals (often below detection threshold), and organic substances. REA-gips is a full-value material used e.g. in the building industry and its properties are comparable to those of natural gypsum.

The synthetic gypsum production was growing in recent years and it reached 2.77 million Mg in 2013. Nearly 20% of that output (0.5 million Mg) is not further processed and has to be dumped on surface storage dumps close to power plants. It is expected that synthetic gypsum production will continue to increase in the next years to come, in connection with the environmental protection requirements. Consequently, higher proportions of unprocessed synthetic gypsum will be dumped (Szlugaj, Naworyta 2015).

A possibility of filling salt caverns with synthetic gypsum presents an alternative to surface storage. Such a solution will allow, on the one hand, to reduce the surface storage facilities and influence positively the preservation of stability of the abandoned caverns on the other hand. Besides, added value will be offered by availability of considerable quantities of commercial brine which presently fills abandoned caverns (Andrusikiewicz 2014). This option will also allow to fulfil the provisions of the Polish Geological and Mining Law which obligate the mining companies to "…secure or liquidate workings…" and "…take indispensable steps to protect the environment (…) after completion of mining operations…"

Current Experiences with Cavern Filling

As mentioned before, caverns are subjected to liquidation after termination of their lifetime, usually by filling with saturated brine. Consequently, the degree of economic cavern use amounts to ca. 85%, with 15% comprising the salt required to obtain fully saturated brine to fill the cavern. To increase the former proportion, brine should be replaced by a different material, with a similar effect as that of brine (Kunstman, Poborska-Młynarska, Urbańczyk 2002). The German engineers possess the best experiences in that area. In several cases, they implemented installations allowing to fill the salt caverns with the materials obtained from industrial or mining processes. Examples are available in such companies as Kavernengesellschaft Stassfurt mbH, DEUSA International GmbH Bleicherode, or Minex plus GmbH which developed and implemented installations for deposition of e.g. drilling slurries, flue-gas-based suspensions, or solid industrial salts. As we can infer from the previous experiences, properly selected mix composition and properly designed filling technologies allow to extract ca. 70-80% of usable brine. In addition, the applicable mixes improve the cavern-wall stability, owing to their aggregate density which is much higher than that of brine. Thus, the rock mass's influence on land surface is reduced.

Conception of Synthetic Gypsum Use for Salt-Cavern Filling

We have assumed for the needs of further considerations that the specific gravity of saturated brine, used for obtaining a specific mix, amounts to 1.202 Mg/m^3, which means that 319.9 kg of salt is dissolved in one cubic metre of brine (kilogram content). The brine proportion is 26.616% and the specific gravity of gypsum is 2.34 Mg/m^3, while that of rock salt is 2.15 Mg/m^3.

It was assumed that a two-phase mix would be produced, composed of gypsum and brine, to be delivered into the salt cavern. The mix pumping process will cause pushing out of pure brine from the salt cavern (Fig. 1). Consequently, it will be necessary to consider a technological process solution to allow mix pumping in the way to avoid uncontrolled mix spread within the cavern. It will be necessary to design a mechanism for the mix to be distributed evenly on the cavern's bottom, with concurrent pump operation optimization, in respect of pumping pressure.

The issue of the rheological properties of the mix is extremely important from the viewpoint of pump operation optimization (Ahmaruzzaman 2010). In the case of the hydro-transportation of mixes with a high degree of compaction, using piping installations, it is necessary to provide a rheological

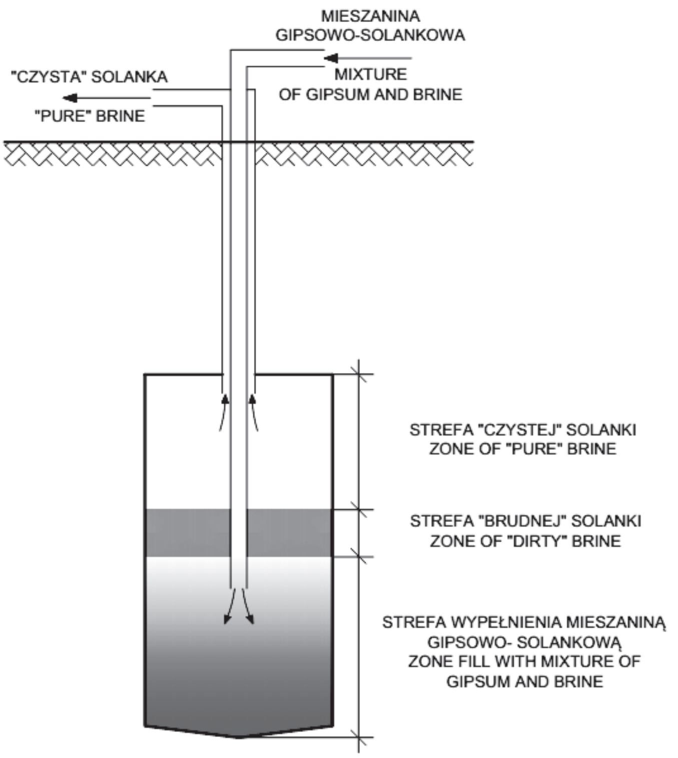

Fig. 1. Diagram of salt-cavern filling with a mix based on synthetic gypsum and fully saturated brine

Rys. 1. Schemat wypełniania kawerny solnej mieszaniną na bazie gipsu syntetycznego i solanki pełnonasyconej

characteristics of the mix to describe the viscosity parameters. Viscosity is in fact that property of the mix which is demonstrated by internal friction forces (resistance) acting against internal mix relocation enforced by external forces. To put it briefly, flow resistance appears during mix transportation in pipelines. The hydro-transport of multi-phase mixes often displays the flow nature which is observed in non-Newtonian liquids. In such a case, it will be necessary to determine a proper rheological model on the basis of determined flow curves. Consequently, it will be possible to design an optimum transportation system (with a selection of pumps and pipe diameters). And since the pipeline diameters are imposed by the technical fittings mounted on the top of the cavern (well head), it remains only to determine the required rheological properties of the mix, which will be the basis of the selection of the best possible brine/gypsum proportion (Malczewska, Czaban, Głowski, Świerzko, Kiwacz, Sobota 2013).

Since the rheological properties of the mix are presently unknown, a purely theoretical analysis has been applied to the mix representing the following brine/gypsum (B/G) proportions by weight: 0.3, 0.4, and 0.5. Considering the fact that saturated brine isused to prepare the mix and the natural water content in gypsum amounts to 7–10%, the prepared mix will show lower proportions. Thus, rock salt leaching will be activated upon contact with the mix. Table 1 below presents indicative water quantities to be introduced to the mix by gypsum. Table 2 shows the proportion of brine contained in the mix, while Table 3 contains the mix's ability to dissolve (leach) salt until original saturation is reached.

Filling of caverns with a mix will activate the leaching process, since the water contained in gypsum will cause a reduction of brine concentration. To prevent that effect, two scenarios are possible. The first one involves the use of previously dried gypsum in the mix to reduce water content and the other one consisting in mix saturation with salt at the stage of mix preparation before it is pumped into the cavern. Both procedures seem to be fairly easy technologically speaking, although cumbersome. What then would be the consequences of pumping an incompletely saturated mix?

In the first filling stage, the cavern bottom will be leached slightly, although temporarily. The bottom layer of the mix filling the cavern will obtain full salt saturation quite quickly (causing increase of its proper gravity) and become a quasi-insulation layer. In that situation, the leaching process will continue in the cavern walls. But also, the

Tab. 1. The quantity of water [kg] introduced by gypsum to the mix, depending on the proportion of the mix and the quantity of water contained in gypsum

Tab. 1. Ilość wody [kg] wprowadzonej przez gips do mieszaniny w zależności od proporcji mieszaniny oraz ilości wody związanej w gipsie

B/G	Water content in gypsum			
	7%	8%	9%	10%
0.3	49	56	63	70
0.4	42	48	54	60
0.5	35	40	45	50

Tab. 2. Mix proportions [%], in connection with the supply of water to the mix by gypsum, depending on the proportions of the mix and the quantities of water contained in gypsum

Tab. 2. Procentowość mieszaniny [%] w związku z dostarczeniem wody przez gips do mieszaniny w zależności od proporcji mieszaniny oraz ilości wody związanej w gipsie

B/G	Water content in gypsum			
	7%	8%	9%	10%
0.3	22.879	22.429	21.997	21.581
0.4	24.087	23.764	23.450	23.144
0.5	24.875	24.644	24.418	24.196

Tab. 2. Mix proportions [%], in connection with the supply of water to the mix by gypsum, depending on the proportions of the mix and the quantities of water contained in gypsum

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S/G	Water content in gypsum			
	7%	8%	9%	10%
0.3	13.04	14.90	16.77	18.63
0.4	11.18	12.78	14.37	15.97
0.5	9.32	10.65	11.98	13.31

process will be slow there because, after saturation of the external mix layer being in contact with the cavern walls, the mix will obtain full saturation quite quickly. Unsaturated particles will have to travel the path which, in an extreme case, will be equal to the cavern's radius. Consequently, the process concentration equalization will continue for an undetermined period of time. No research has been conducted on the caver-wall leaching mechanism, with the use of the mixes discussed here, and that is why no data are available.

As a continuation of the above-described purely theoretical considerations, we analyzed the situation or rather the consequences of supplying a mix with incomplete salt saturation into the cavern. The following assumptions were made:

- the cavern radius r – 25 m
- the studied section h – 1 m
- the mix density γ (for B/G = 0.4) – 1.885 Mg/m³
- the water content in gypsum – 8%
- the leaching ability – 12,78 kg of salt/m³ of mix

The following were calculated in respect of the above data:

- the section volume V – 1,963.5 m³
- the cavern wall surface area in contact with the mix – 157.1 m²
- the weight of the suspension filling the section – 3,701.2 Mg
- the ability of salt leaching at the section – 47.3 Mg;
- the volume of salt to be leached – 25.1 m³
- the leaching depth Δr – 15.9 cm

The above values should be treated as indicative because they do not take into account the

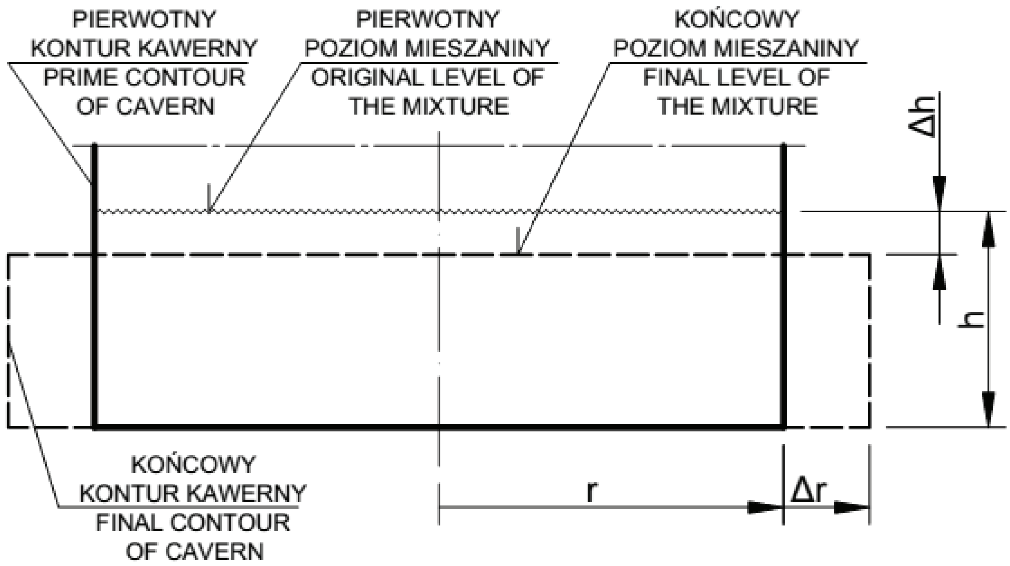

Fig. 2. A simplified diagram of the consequences of pumping the mix based on synthetic gypsum and saturated brine into the cavern

Rys. 2. Uproszczony schemat skutków załaczania do kawerny solnej mieszaniny na bazie gipsu syntetycznego i solanki nasyconej

effects consisting in the mix-mirror lowering, in connection with the change of the cavern diameter or the so-called volumetric contraction (a physical phenomenon consisting in the change of solution or mix volume as a result of intermolecular reactions between the mix components).

A further analysis of the phenomena mentioned above will allow us to determine that the increase of the cavern diameter as a result of wall-cavern leaching will cause reduction of the mix mirror by 12.78 mm, and, taking into account the contraction mechanism (which amounts to ca. 4% for salt), the final reduction value will be Δh ≈ 13.32 mm (Fig. 2). Those are fairly low values, considering the cavern height. However, when filling the cavern with a gypsum mix to a theoretical height of e.g. 500 m, the mix-mirror level will be ca. 6.66 m, reflecting the cubic capacity of more than 13,200 m³, which will in turn require nearly 25,000 Mg of the mix!

Conclusions

As we can infer from the above considerations, the conception of salt cavern filling with gypsum mixes, based on saturated brine, is the direction worthy of our interest. Synthetic gypsum used as the base of the mix is available in large quantities and its overproduction will even increase in the next years to come. Salt caverns seem to be good alternatives in respect of surface storage areas where ca. 0.5 million Mg of that product is dumped annually. The use of synthetic gypsum for the cavern filling purposes offers many advantages, including the following:

- undoubtedly, the method will improve the long-term stability of caverns;
- the method will allow to reduce the synthetic-gypsum surface storage-facility capacities;
- non-toxic synthetic gypsum will allow to recover considerable quantities of saturated brine contained in caverns, with the application of properly selected filling technologies; it is estimated that the recovered amount can be equivalent to 80% of the cavern volume;
- non-toxic synthetic gypsum does not present any hazard to the geological environment;
- the method does not require considerable capital investments associated with the filling technology or generally understood industrial safety;
- the mix is easy to transport, even at large distances;
- the method can become a source of potential income generated by acceptance of synthetic gypsum for underground storage.

The management of surplus synthetic gypsum production by mining technologies, to fill salt caverns in the case under discussion, is an ecological activity which is hardly invasive for the environment.

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Możliwość wykorzystania gipsów syntetycznych w likwidacji kawern solnych

W wyniku procesu mokrego oczyszczania spalin powstających w trakcie spalania węgla otrzymuje się duże ilości gipsu syntetycznego, który jest pełnowartościowym produktem możliwym do wykorzystania gospodarczego. Jednak jego nadprodukcja czyni, że duża część trafia na składowiska powierzchniowe. W artykule przedstawiono możliwość wykorzystania gipsu do sporządzania mieszanin na bazie solanki pełnonasyconej i wypełniania nią zlikwidowanych kawern solnych. Zabieg taki pozwala z jednej strony na odzyskanie pełnowartościowej solanki wypełniającej kawernę, z drugiej zaś ogranicza ilość gipsu trafiającego na składowisko powierzchniowe. Ponadto wypełnienie kawerny mieszaniną gipsową jest od strony geomechanicznej korzystniejsze, niż wypełnienie solanką. Omawiany sposób wypełniania kawern solnych ma także walor związany z ochroną środowiska.

Słowa kluczowe: kawerny solne, gips syntetyczny, likwidacja kawern, ochrona środowiska