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Geochemical and Geotechnical Aspects of high temperature thermal energy storage in soil

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Abstract

In this paper an overview is attempted over geo-/hydrochemical, hydrogeological and geotechnical problems which eventually may affect the use of high temperature thermal energy storage in the ground. Beneath 80 °C moisture reduction and dissolution as well as precipitation of some elements and minerals is regarded, above 80 °C in addition the effects of desorption of water from clay minerals, dehydration of gypsum and structural decomposition of specific clay minerals have to be considered.

For the application of high temperature thermal energy storage in the ground an intensive geological evaluation of proposed sites is essential to avoid problems. More work is to be done to identify and develop methods and techniques (including geophysical investigations) for easy and reliable site evaluation.

Kurzfassung

In diesem Artikel wird versucht, einen Überblick über geo-/hydrochemische, hydrogeologische und geotechnische Probleme bei der Anwendung von Hochtemperatur-Wärmespeicherung im Erdreich zu geben. Unter 80 °C sind Austrocknung sowie Lösung und Ausfällung einzelner Elemente und Minerale zu beachten, über 80 °C kommen die Abgabe adsorbierten Wassers aus Tonmineralen, die Dehydration von Gips und die Zerstörung spezieller Tonminerale hinzu.

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Für die Nutzung von Hochtemperatur-Wärmespeicherung im Erdreich ist eine eingehende geologische Untersuchung geplanter Standorte unerläßlich. Weitere Arbeiten sind erforderlich, um einfache und verläßliche Methoden (einschließlich geophysikalischer Erkundung) für die Standortbeurteilung zu benennen bzw. zu entwickeln.

Introduction

Earth as heat source, heat sink or storage medium in combination with heat pumps has been discussed and tested sinces the late 1940's (e.g. KEMLER, 1947; GUERNSEY *et al.*, 1949; INGERSOLL *et al.*, 1950; VESTAL & FLUKER, 1957). Vertical heat exchangers in soil and rock are used since the late 1970's to extract heat from the ground as heat source for Ground Coupled Heat Pumps. In this application, temperatures in the ground vary from -5 to 10 °C. Reversible heat pumps use the ground as heat sink, thus raising ground temperatures in the close vicinity of the heat exchanger to 25 °C and above (BOSE *et al.*, 1985). Earth probe systems also have been applied to thermal energy storage (seasonal storage of solar thermal energy, MÜLLER *et al.*, 1986; in horizontal coils BRUCK *et al.*, 1981) and to cold storage for space cooling (SANNER, 1990). Most scientific work related to this plants emphasized on low to medium temperatures (up to 25-40 °C), including problems with freezing of soil and groundwater.

Applications in cogeneration or waste incineration (ANDERSSON, 1988) as well as high temperature solar thermal energy require higher storage temperatures. When considering thermal energy storage in soil using vertical heat exchangers (boreholes, earth probes, "ducts") some problems may arise at higher temperature levels (40 - 90 °C). Those problems can be summarized as follows:

Hydro-/geochemical and hydrogeological problems

- Equilibrium of phases containing Silicon, Iron and Aluminum
- Other water-rock interactions
- Clogging of open fissures with Al/Fe Hydroxides or Calciumcarbonate

Problems related to specific minerals

- Clay, removal of adsorbed water
- Clay, structural decomposition
- Gypsum / Anhydrite

Geotechnical problems

- Heaving of the surface
- Shrinking of the soil and land subsidence

The list may be not complete, and some of the mentioned problems may prove to be negligible. In this paper an attempt is made to characterize the problems and to give an overview of the current status of investigation in this field.

It is presumed the soil pores are filled with water at least partially. Porous sediments in non-saturated conditions have poor thermal properties, so from that point of view a site for thermal energy storage would preferably be choosen in a soil with high water content (high specific heat of water!). Hence water as medium for alterations can be considered as always present.

Hydro-/geochemical and hydrogeological problems

Equilibrium of phases containing Silicon, Iron and Aluminum

The majority of rocks and sediments is composed of silicates, quartz and aluminosilicates (clay minerals). Hence the equilibrium of silica and aluminum in minerals and pore water is vital for all processes in the soil. Silicates can be decomposed in the presence of groundwater, in particular feldspars, mica and olivine tend to loose silica and enrich relatively in aluminum.

Iron, which is to be found in olivin, pyroxen and garnet, can be mobilized and precipitates later as e.g. α-FeOOH (goethite); aluminum, potassium and sodium from feldspares (e.g. albite) precipitates as $Al(OH)_3$ (gibbsite) and kaolinite (GARRELS & HOWARD, 1959; PETROVICH, 1986; ZELLMER & WHITE, 1986), e.g.:

$$\underset{\text{orthoclase}}{2\,KAlSi_3O_8} + 3\,H_2O = \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 4\,SiO_2 + 2\,K^+ + 2OH^-$$

McKINLEY *et al.* (1988) experimented with water circulated through sandstone (Ironton-Galesville-formation, paleozoic), consisting of quartz and some feldspar. The time- and temperature-dependent enrichment of the solution in silicon and potassium is given in Fig. 1. A mobilization of both elements can be seen, the effect is stronger for Si with increasing temperature.

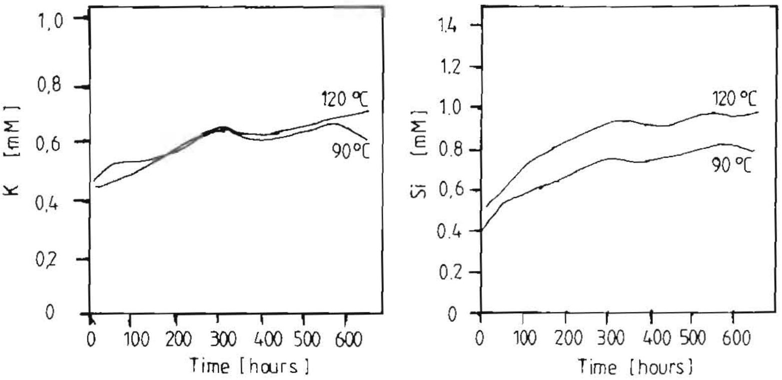

Fig. 1 *Si- and K-content in water circulated through sandstone (after data from McKINLEY et al., 1988)*

Aluminum minerals (gibbsite, boehmite, diaspore, corundum) show solubility as aluminate ion, $Al(OH)_4^-$, in aqueous solutions:

$$\underset{\text{corundum}}{Al_2O_3} + H_2O = \underset{\text{diaspore}}{2\ \alpha\text{-}AlOOH}$$

$$\underset{\text{diaspore, boehmite}}{\alpha\text{-}, \gamma\text{-}AlOOH} + H_2O + OH^- = \underset{\text{aluminate ion}}{Al(OH)_4^-}$$

$$\underset{\text{gibbsite}}{Al(OH)_3} + OH^- = \underset{\text{aluminate ion}}{Al(OH)_4^-}$$

The solubility is higher in alkaline groundwater and raises with temperature. APPS *et al.* (1986) found the dissolution kinetics of boehmite and diaspore to be rather slow at temperatures below 100 °C. Similar solubility characteristics can be found with α-FeOOH (goethite) and γ-FeOOH (lepidocrocite). Due to the temperature dependance of the process, Al and Fe is mobilized when the ground is heated and precipitates on temperature decrease. Though this does not much effect the overall strength and fabric of the soil, the precipitation in the cooler zones in some distance from the heat exchanger can result in clogging of pores and reducing soil permeability for groundwater.

Other water-rock interactions

It is well known, that solubility of calcite depends on the amount of CO_2 available to form HCO_3^--ions. This results in lower solubility at higher temperatures (RUCK *et al.*, 1990). WOLF *et al.* (1986) show, that the solubility in water rich in NaCl at 60 °C is about half the value as at 25 °C. The consequence would be precipitation during loading of the store and mobilization during heat recovery.

Interaction of water with sandstone is described by McKINLEY *et al.* (1988), and McCARTNEY (1986) deals with the interaction of water and granite. In all cases mineral phases are mobilized and precipitate later. Higher temperatures increase mobilization. McCARTNEY (1986) points out, that "*by circulating a typical low salinity, surface water through a granite host rock at 60-80 °C, irreversible reactions are induced...*". Those reactions include formation of smectite and chlorite from a plagioclase, biotite and fluorite sample. The resulting minerals are much less in strength than the source material and may be transported with groundwater flow. The principal reactions are (underlined = precipitation):

$$\begin{aligned}&\text{plagioclase} + \text{biotite} + \text{fluorite} + Mg^{2+} + K^{+} + Fe^{2+} + Mn^{2+} + H^{+} + H_2CO_3 \\ &\quad \dashrightarrow \underline{\text{K,Mg-smectite}} + \underline{\text{Fe,Mg-chlorite}} + \underline{Fe(OH)_3} + \underline{Mn_3O_4} + Ca^{2+} + Li^{+} \\ &\quad\quad + Na^{+} + H_4SiO_4 + F^{-} + Cl^{-} + HCO_3^{-}\end{aligned}$$

On temperature increase (25 - 80 °C):

$$Ca^{2+} + CO_3^{2-} \dashrightarrow \underline{CaCO_3}$$

In presence of sulphides (pyrite):

$$4\,FeS_2 + 15\,O_2 + 14\,H_2O \dashrightarrow \underline{4\,Fe(OH)_3} + 8\,SO_4^{2-} + 16\,H^{+}$$

The use of warm water to mobilize minerals is shown in NORDELL *et al.* (1988), where leaching experiments in the Luleå borehole store are described. A strong dependance of silicon dissolution on temperature has been found in laboratory experiments with crushed rock (figure 2).

For calculating stability of ions and minerals in rock and water some computer programs have been developed: PHREEQUE (PARKHURST *et al.*, 1980) and WATEQ-F (PLUMMER *et al.*, 1976). An example of the application of WATEQ-F to describe groundwater chemistry is given in SANNER *et al.* (1986). WATEQ-F works well at temperatures up to app. 50 °C; a high-temperature version called MINTEQ has been developed recently (E.A. JENNE, personal communication). This programs can help to qualify effects of temperature changes to the stability of mineral phases in given soil- and groundwater-chemistry.

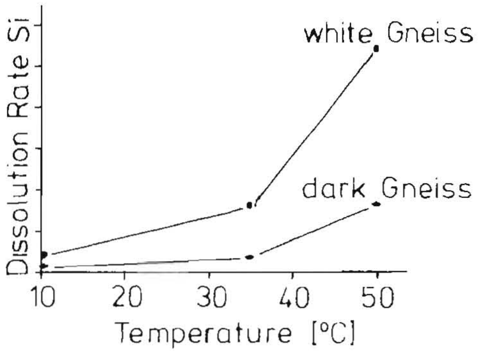

Fig. 2: *Dependance of Si dissolution rate (arbitrary units) on temperature (after data from NORDELL et al., 1988)*

Clogging of open fissures

Mobilization and precipitation of most elements will widen pore space in the vicinity of the heat exchanger and will close it in some distance. For carbonates the reverse process should be expected; as consequence, in heated zones content in Si, Fe, Al, K etc. will decrease and carbonate will be enriched. Natural ground water flow will be influenced or inhibited. For storage purposes this may be considered as advantage, because heat loss due to ground water flow could be reduced.

Problems related to specific minerals

Clay, removal of adsorbed water

Clay minerals, in particular those of the 3-layer or mixed layer type, are able to adsorb water. This water is desorbed at higher temperatures than normal soil moisture and needs longer to be restituted. The presence of adsorbed water increases the volume of such clay particels, in the case of some bentonites it is nearly doubled. In reverse, removal of adsorbed water leads to additional shrinking, which is irreversible in short terms.

The desorption must not be confunded with dehydroxilation of clay minerals, which takes place at higher temperature levels (500-600 °C for kaolinite and up to 700 °C for Montmorillonite, figure 3).

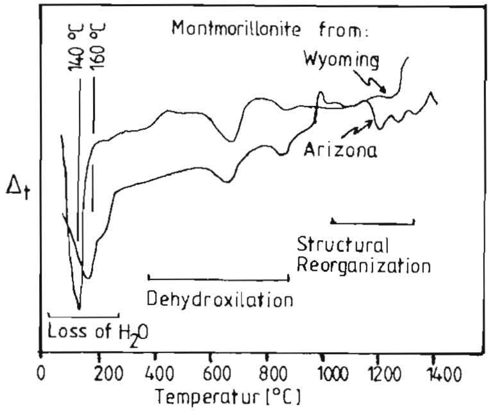

Fig. 3: *DTA-curves for two types of montmorillonite (after data from EARNEST, 1981)*

Though desorption should not take place at the desired temperatur level for storage, locally the begin of such processes close to the heat exchanger cannot be excluded. At temperatures up to 80 °C some micas have also the ability to adsorb water in a reversible, very slow process, but macroscopic effects are negligible (WEISS *et al.*, 1956).

Tab. 1: *Dehydration temperatures for adsorbed water (after data from EARNEST, 1980, 1981 and MACKENZIE & CAILLERE, 1979)*

Clay name	provenience	desorption temp.	water loss
Black Hills Bentonite	USA, Wyoming	130-150 °C	4,99 %
Cheto Montmorillonite	USA, Arizona	160-200 °C	ca. 10 %
Attapulgite	USA, Florida	160 °C	12.96 %
Kaolinite Standard	USA	110 °C	0.26-0.74 %

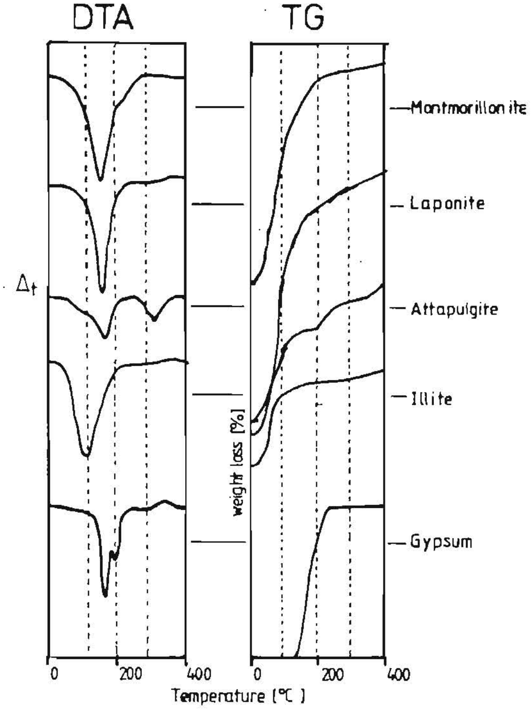

Fig. 4: *DTA- und TG-curves for some clay minerals and gypsum (after data from MACKENZIE & CAILLERE, 1979)*

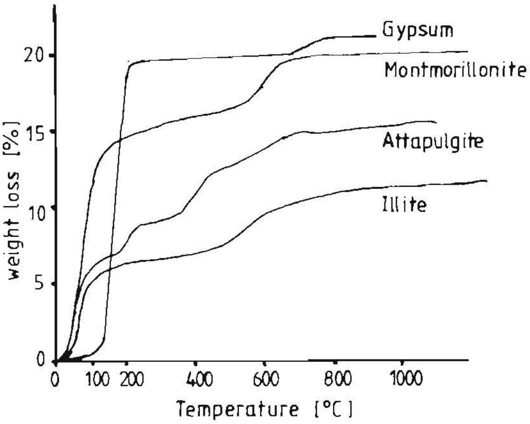

Fig. 5: *Weight loss when heating for some clay minerals and gypsum (after data from MACKENZIE & CAILLERE, 1979)*

Clay, structural decomposition

The clay mineral halloysite is very sensitive to increased temperatures; at 70 °C the so-called 10-Å-halloysite, $Al_2Si_2O_5(OH)_4 \cdot 2\,H_2O$, passes to 7-Å-halloysite (dehydrate), $Al_2Si_2O_5(OH)_4$, a process which is irreversible. In laboratory the process is completed after heating a sample to 100 °C for app. one hour. At higher temperatures the mineral is disordered completely (fig. 6).

Vermiculite-type clay minerals also show narrowing of lattice spacing at 110 °C, but the mineral remains stable up to 550 °C.

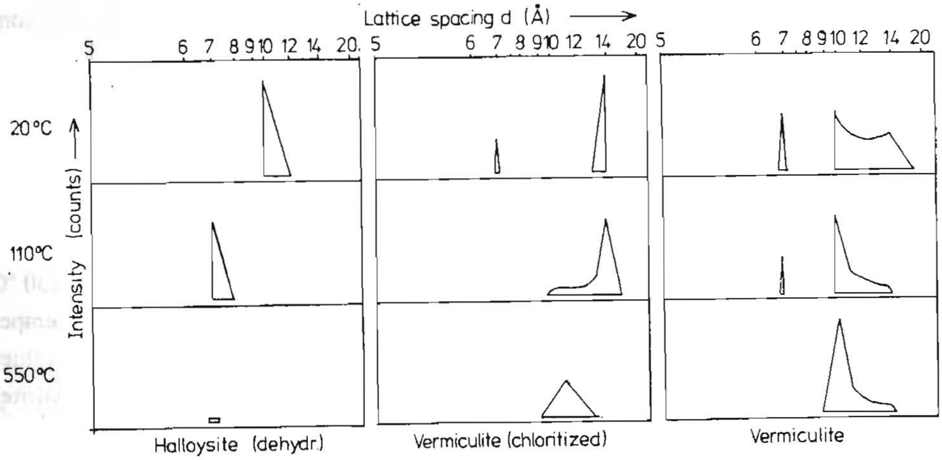

Fig. 6: *Lattice spacing of some clay minerals at different temperatures (after data from THOREZ, 1975)*

Gypsum, Anhydrite

The system $CaSO_4$ - H_2O has several stable or metastable phases. These minerals and their properties are listed in table 2.

Tab. 2: Properties of CaSO4 - H2O - phases (after data from SCHWIETE & KNAUF, -)

Mineral name	formula	crystal system	spec. weight	water content
Gypsum	$CaSO_4 \cdot 2\,H_2O$	monoclinic	~ 2.32 g/cm^3	20.92 %
α-Hemihydrate	$CaSO_4 \cdot \frac{1}{2}\,H_2O$	orthorhombic	2.76 g/cm^3	6.2 - 8.0 %
β-Hemihydrate	$CaSO_4 \cdot \frac{1}{2}\,H_2O$	orthorhombic	~ 2.63 g/cm^3	6.2 - 12.0 %
α-Anhydrite III	$CaSO_4$	hexagonal	2.59 g/cm^3	0.02 - 0.05 %
β-Anhydrite III	$CaSO_4$	hexagonal	2.48 g/cm^3	0.6 - 0.9 %
Anhydrite II	$CaSO_4$	orthorhombic	~ 2.95 g/cm^3	0.0 %
Anhydrite I is formed at temperatures above 1180 °C				

Gypsum is changed to anhydrite by loss of water; this effect takes place at temperature levels close to those of the discussed storage. A reduction in volume is the consequence. The dehydration reactions are:

	177 °C <--	α-anhydrite III	100 °C <--	α-hemihydrate	97 °C <--	
anhydrite II						gypsum
	400 °C <--	β-anhydrite III	107 °C <--	β-hemihydrate	45 °C <--	
	slow -->		slow -->		fast -->	

The dehydration is also obvious in DTA diagramms; in figure 4 two peaks at 130 °C and 190 °C can bee seen. In natural conditions the above reactions start at lower temperatures (~80 °C), depending on the environment and the type of gypsum. Some values are given in table 3. For the reverse process (formation of gypsum from anhydrite) HUDER & AMBERG (1970) record an increase in volume of app. 60 %.

Tab. 3: Dehydration temperatures and weight loss for some gypsum samples (after data from MACKENZIE & CAILLERE, 1979)

Sample	Temperature range	weight loss	total weight loss up to >600 °C
F5	20 - 120 °C	19.5 %	22.3 %
B3	20 - 230 °C	19.0 %	21.8 %
GB7	20 - 120 °C	19.1 %	21.1 %
EIR1	20 - 120 °C	18.5 %	20.5 %

Gypsum and anhydrite are natural constituents of evaporitic sediments. With increasing salinity of marine water precipitation of dolomite, gypsum, anhydrite, halite, sylvine etc. occures. In table 4 the most important $CaSO_4$-bearing sediments in Germany are listed. A content of gypsum or anhydrite is also frequent in shales, marls, limestones and similar sediments.

Tab. 4: Major gypsum- or anhydrite-containing strata in Germany

Epoch	Northern Germany	Southern Germany	Alps
Cenozoic		Anhydrite and salt in the Upper Rhine Graben, Eocene to lower Oligocene	
Mesozoic	Gypsum and salt, mid Keuper (Karn)	Gypsum, "Gipskeuper", mid Keuper (Karn)	Anhydrite, Karn
	Anhydrite, gypsum, mid Muschelkalk (Anis/ Ladin)	Anhydrite, gypsum, mid Muschelkalk (Anis/ Ladin)	
	Gypsum, "Röt-Salinar" upper Buntsandstein (Skyth)		Anhydrite, Skyth/Anis
Paleozoic	Anhydrite, salt, Zechstein (upper Perm) salt diapirs!		

Geotechnical problems

Heaving of the surface

Due to heating of the ground vapor pressure of pore water increases. In deep aquifers as in Thiverval-Grignon the overburden pressure is high enough to prevent boiling, but some heaving was detected, and the well casing was pushed up app. 20 cm at the end of a 170 °C loading cycle (J. DESPOIS, personal communication). In shallow holes as may be used for duct storage, vapor should find a way to the surface through pores and fissures, thus reducing overpressure. However, boiling of pore water has to be prevented; a large quantity of vapor would need too long to migrate to the surface and heaving could occure.

Shrinking of the soil and land subsidence

When removing water, soil volume decreases. Up to 105 °C mainly normal soil moisture is reduced, above this temperature an influence of dehydration of adsorbed or intracrystalline water can be found (3-layer clay minerals, gypsum etc.). Shrinking is dominant in fine-grained soils as silt and clay.

Tab. 5: Shrinking ratio of some clays when dryed (after data from REUMANN, 1968)

Clay name	provenience	Shrinking ratio (by volume)
Wildstein Blue Clay	CSFR	6.2 %
Hirschau Kaolin	FRG, Oberpfalz	1.8 - 5.0 %
Westerwald Clay	FRG, Westerwald	3.4 - 6.2 %
Meissen Clay	GDR	5.8 - 7.4 %
Halle Clay	GDR	2.2 %
China Clay	England	2.7 - 4.6 %
Ball Clay	England	3.2 - 5.9 %

To the shrinking effect due to decreased soil moisture the effect of desorption processes at higher temperatures (100-200 °C) is added. ASHRAF (1981) tested samples from a profile in the tertiary Esna-shales, Egypt. Swelling of laterally confined dry samples, supplied with deionized water, has been measured. In table 6 semiquantitative mineral composition and swelling ratio (in percent of the original sample height) is given. This gives an impression of possible soil compaction when the reverse process is considered. The highest swelling ratio is obtained in the samples with the highest content of anhydrite (ES 2, ES 7).

Tab. 6: Swelling ratio by height for Esna-shales (after data from ASHRAF, 1981)

Sample	Kaolinite	Illite	Montmor.	Carbonates	Anhydrite	Swelling ratio
ES 1	~ 47 %	-	~ 20 %	5.3 %	9.3 %	33.3 %
ES 2	~ 41 %	-	~ 18 %	9.9 %	14.6 %	39.0 %
ES 3	~ 51 %	~ 12 %	~ 14 %	3.8 %	7.9 %	28.4 %
ES 4	~ 38 %	~ 21 %	~ 13 %	6.1 %	9.5 %	27.6 %
ES 5	~ 31 %	~ 11 %	~ 11 %	26.4 %	12.0 %	33.0 %
ES 6	-	~ 23 %	~ 25 %	20.3 %	10.0 %	36.6 %
ES 7	-	~ 26 %	~ 18 %	22.2 %	13.5 %	40.0 %

Shrinking opens fissures, and in non-saturated circumstances thermal conductivity as well as specific heat is reduced substantially.

Conclusions

Tab. 7: Summary of ground-related problems of high temperature thermal energy storage

Temperature range	Phenomenon	Consequence
40 - 80 °C	moisture reduction	deterioration of thermal properties of the ground, surface subsidence
	mobilization of Si, Al, Fe and precipitation of carbonate	opening resp. clogging of pores and fissures
above 80 °C	desorption of adsorbed water in clay minerals, dehydration of gypsum	shrinking, open fissures, surface subsidence
	structural decomposition of some clay minerals	

Geochemical and hydrochemical problems are the same as in geothermal systems or high temperature ATES. The advantage of borehole (or "duct") storages is the use of heat exchangers in the ground, thus preventing sensible parts as pumps from being destroyed by scaling or corrosion. Geochemical and hydrochemical alterations will affect composition and permeability of the soil. The thermodynamic properties can be changed as well as the natural ground water flow rate, but severe geotechnical problems due to geochemical reactions must not necessarily occur.

Shrinking of clay minerals and gypsum as well as thermal dilatation of rock will affect the site itself. Shrinking of a soil is controlled by type and amount of clay minerals and gypsum. In poor and very poor conditions (high content in 3-layer clay minerals or high gypsum content) soil moisture reduction by heating of the ground will result in surface subsidence. Shrinking also affects thermal properties. Gypsum has a substantial decrease in volume when forming anhydrite. Since this begins at ~80 °C, soils with gypsum content should be avoided.

Surface heaving induced by vapor pressure should be prevented by restricting temperatures at app. 80 °C. The effect of material dilatation seems to be negligible.

Further emphasis in investigation should be given to the change of thermal properties due to chemical and mineralogical alterations and drying/shrinking processes. Impact on natural ground water flow should be investigated as well as surface subsidence due to drying/shrinking processes.

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