GAS PRODUCTION AND TRANSPORT IN A SALINE ENVIRONMENT - WHAT IS DIFFERENT TO OTHER HOST FORMATIONS?

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ABSTRACT

Gas production in and around waste seems to be quite independent from the kind of host formation where the waste is disposed. There exist, however, remarkable differences which have eventually led to misinterpretations. This is especially true for salt. Scenarios in salt, where gas production becomes relevant, have to assume some kind of faulted conditions because of the low water content and the low permeability of salt. Thus such scenarios are not a priori defined but have a probability of occurrence of less than one. Since the starting point of such events and their boundary conditions are not exactly known, parameter variations have to be performed to establish worst case situations or a probability distribution function. The tightness and the plasticity of salt enable pressure buildup which interacts with the geomechanical forces and the fluid flow. These variable boundary conditions require a high modelling effort. The different gas formation mechanisms are influenced in salt by the lack of water, the different kind of groundwater (brines) that have to be considered, possible phase transitions between water and steam and higher close dose rates compared to other host formations. Modelling of gas transport in salt normally is confined to the engineered barriers as pathway. This enables countercurrent flow of gas and brine and enhancement of nuclide migration by gas flow in concurrent flow. The conclusion is that comparisons of results require careful assessment of the specific of each host formation and the derived design requirement of the repositories.

INTRODUCTION

Gas production in and around radioactive wastes is considered a safety issue in all kind of host formations. Therefore most of the technical problems associated with gas in a repository are discussed rather independent from the kind of host rock, in which the waste is placed. Nonetheless there exist some remarkable differences in gas formation and transport behavior between different host rocks. This is especially true for salt as a host formation. Since this has given rise to occasional misunderstandings and misinterpretations it seems worthwhile to contrast the situation in a saline environment with other formations.

SCENARIOS

Gas formation requires for nearly all formation mechanisms water. If compared, however, with other host rocks salt has the lowest water contents and the lowest permeabilities (Table I). Therefore not only the water available around the waste but also the possible water supply by transport processes in salt is limited. It is for this reason that long-term safety analyses for waste repositories in salt often have to assume accident scenarios or some kind of faulted conditions to produce a scenario where gas production becomes relevant.

Fissured material like crystalline rock in contrast permits the groundwater to flow into the repository and produce inundated conditions as the normal situation. Clay as another alternative as host formation contains much moisture and even needs it to sustain its tightness.

This means that the starting point for safety considerations concerning gas formation in a salt repository may be quite different to other hosts. If an event has to be postulated as starting point neither time nor boundary conditions are completely known. Therefore calculations cannot be performed straight forward, but must be repeated with parameter variations in order to perform a sensitivity analysis and if possible to produce a conservative scenario. Since the required accident conditions are of geological nature it becomes difficult to define precise boundaries for these parameter variations. For example location and nature of the fault, where brine inflow is postulated, can often only be argued with plausibility considerations. Thus the gas problem in salt is primarily to define either a conservative, but still plausible scenario or a reasonable probability distribution function. And it is only in the second place that accuracy of source term definition or calculational issues for gas transport assessment become important.

Since salt in addition has a good heat conductivity the allowable temperature for the waste can be rather high. Design values considered are in the range of 150 to 300°C and are limited by the decomposition temperature of halite and - to a minor extent - of possible carnallite inclusions. Therefore high active wastes can be disposed in higher concentrations resulting in a reduced demand of storage volume required. On the other hand higher activity concentrations and thus temperatures can aggravate conditions for gas production by corrosion and radiolysis. So one has to balance this disadvantage against the profits.

The better plastic behavior of salt compared to other host formations causes the salt to creep onto the waste with a rather high convergence rate. This reduces open spaces and closes possible pathways for water intrusion even if they are arbitrary postulated. In the case of high active waste this can be used to demonstrate that only a few years are necessary to prevent any brine inflow into the disposal area of a repository.

However, reduction of void volume together with low permeabilities can cause higher gas pressures. The required modelling effort under these circumstances, i.e. moving boundary conditions due to interaction between gas pressure and lithostatic pressure is considerable.

In summary the influence of gas on scenarios in salt may look quite different from those in other host formations since

TABLE I

Characteristic Properties of Different Host Formations

Parameter	Salt (pure halite)	Granite	Clay	Tuff
Water contents (%)	0.005-0.05 (domed) 0.1-0.5 (bedded)	0.1-1	15-20	0.1-1 (saturated)
Permeability (m^2)	$< 10^{-22}$	10^{-17}-10^{-18}	10^{-21}-10^{-23}	10^{-15}-10^{-16}
Porosity	0.001-0.01	0.05-1	0.3-0.5	20

- the scenarios in general are not a priori defined but have to be derived from parameter variations for postulated plausible starting events;
- the starting events are of probabilistic nature, i.e. they occur only with a certain probability less than 1;
- the gas source term is reduced by lack of water, but may be enhanced by higher activity concentrations and temperatures;
- modelling efforts for transport calculations are higher because of the strong coupling between gas pressure buildup and the creep behavior of the salt.

GAS FORMATION

Corrosion

Corrosion is a mechanism, which is very sensitive to physical and chemical conditions in the repository. Therefore e.g. temperature and groundwater chemistry may have a strong influence on gas formation by anaerobic corrosion. Table II summarizes the main constituents of different groundwater in host formations. As can be seen the dominating species as well as those most relevant for corrosion, like $CO_3$2-, $SO_4$2-, Cl^-, are distributed quite different. Accordingly corrosion rates are spread over about one decade. Table III shows a comparison of anaerobic corrosion rates for temperatures around 100°C. Gas formation rates can be calculated from these rates from the stoechiometric ratios of the reaction equations. Higher rates may, however, not only result from higher contents of critical ions but can also be associated with shorter measurement periods where the protective layer of corrosion products was not yet fully developed.

For salt, the situation is more complex. If normal humidity in salt is considered as the corrosive agent, NaCl brine is the typical composition. If, however, accidential brine inflow from water bearing formations outside the host rock is assumed, $MgCl^2$ rich brines like Q brine are more appropriate. Q brine is hydrolysed at higher temperatures (≥ 90°C) to HCl and $Mg(OH)_2$. The consequence is a decrease of the pH value to about 3 to 5 which means that acid corrosion at rather high rates takes place.

Except for the Q brine it seems, however, salt does not exhibit a generally different behavior with regard to gas formation from corrosion. If we now include the temperature as parameter for corrosion rates the above mentioned difference in maximum temperatures becomes relevant. For granite and clay, for example, 100°C are in most countries used as an upper limit. Only for tuff, basalt and salt higher values have been suggested and applied. For the first two because of their fissured nature liquid water should never exist above 100°C for extended periods. Thus steam corrosion takes place under high temperature conditions with reduced corrosion rates compared to inundated conditions. Only in unsatured environments this advantage may be partly compensated by the presence of oxygen with accordingly higher rates.

In salt the tightness of the host formation enables the development of higher pressures under which liquid water can exist above 100°C. Therefore pressure calculations have to be included in the assessment of the correct corrosion rate at given boundary conditions.

TABLE II

Main Components of Groundwaters in Different Host Formations (in ppm)

Ion	Salt NaCl brine	Salt Q brine	Granite	Tuff	Clay
Na^+	120 000-150 000	7 000	0-5 000	50	60
K^+	1 500	32 000	50-100	5	7
Mg^{2+}	340	90 000	0-15	2	4
Ca^{2+}	1 400	-	10-1 100	15	20
Fe^{2+}	-	-	0.02-5	0.04	190
Cl^-	200 000-250 000	270 000	0-8 000	5-10	35
SO_4^{2-}	5 000	15 000	0-2 000	20	-
CO_3^{2-}	-	-	100-300	120	190
F^-	-	-	0-4	2	820
pH (25°C)	6	5	7-9	7	7-8

For high level waste higher temperatures are connected with rather high radiation levels around the waste, if thin-walled containers are used or container failure has to be assumed. For vitrified wastes in containers intended for borehole disposal for example dose rates of up to 10 kGy/h at the outer container wall are specified. This may cause the formation of aggressive radiolysis radicals which enhance corrosion. Experimental evidence shows that the presence of water is decisive for this effect.

In salt the most marked enhancement of corrosion is observed compared to other formations. This difference increases if lower temperature limits are applied and the dose rates decrease accordingly, thus making radiation an influencing factor of negligible importance. Values of experience are included in Table III.

So far all corrosion rates discussed have been measured in laboratories. If we recall that salt is rather dry and tight a check has to be made if these rates can be expected under realistic conditions in a salt repository. Experimentally this was performed in the Asse salt mine Brine Migration Test (BMT). In this experiment materials emplaced in salt in four vertical boreholes were heated up to more than 200°C. Two of the boreholes furthermore contained Co 60 sources which produced a dose rate of 0.3 kGy/h. Test duration was about two years. The results are shown for two materials in Table IV. In situ corrosion rates were a factor of 20-30 lower than those measured in laboratory experiments. This is certainly due to a lack of water. But furthermore the available water must have been less effectively consumed compared to the inundated conditions simulated in the laboratory.

In summary corrosion rates are comparable for different host formations under undisturbed laboratory conditions below 100°C. This situation may be changed, if

- water availability is restricted,
- Magnesium rich brine inflow is assumed in salt due to accidential brine inflow,
- phase transitions have to be considered, or
- dose rate effects become relevant.

Radiolysis

Radiolysis in host formations can become relevant in general only for high active wastes. Normally gas production from this source can be limited by thick-walled containers whose shielding effect reduces doses outside to insignificant levels. In the long term, however, container failure has to be assumed and groundwater may come into close contact with the waste. In this case radiolysis of water is a relevant process. There seems to be not much difference in this case between different formations. But again a second look may change this view.

First another time water supply is decisive since water is the most important material that can be decomposed by radiolysis. Therefore measured $G(H_2)$ values are spread according to the broad range of water contents in host formations. In Fig. 1 a comparison is given. The $G(H_2)$ value for crystalline rock has been calculated for water radiolysis with the assumption of 0.2 % water contents as measured values were not available. All other values have been measured.

Under undisturbed conditions in salt radiolysis takes place in competition with other gas formation processes like corrosion. As just has been demonstrated corrosion is able to consume the available water within a few years. Therefore, when radiolysis starts no more water may be present.

On the other hand if thin-walled containers are used, whose failure may be assumed within a short time after emplacement, a balance for water has to be set up to describe the competing processes of corrosion and radiolysis.

If accidential brine inflow is assumed the situation becomes more comparable to other formations. The only peculiarity of salt in this situation is that complex brines behave somewhat different from pure water or most other groundwaters with respect to radiolysis. Experiments have shown, that the combination of high chloride and sulfate concentrations can produce synergistic effects resulting in higher equilibrium

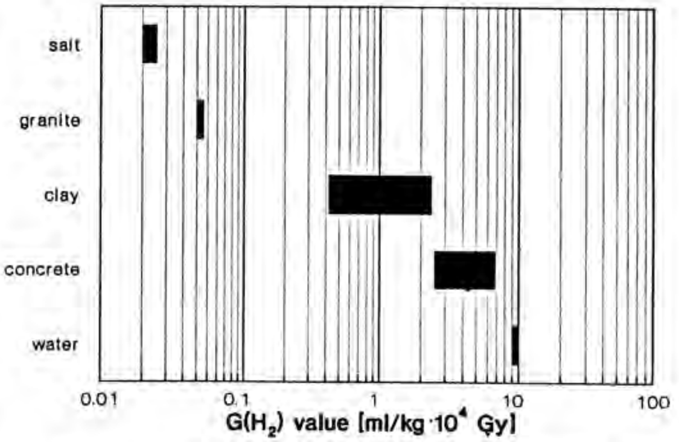

Fig. 1. Radiolytic gas formation rates (β/γ - radiolysis).

TABLE III

Anaerobic Corrosion Rates (in μm/a) of Different Metals in Groundwaters of Potential Host Formations for Temperatures Around 100°C

Material	NaCl brine	Q brine	Granite	Tuff	Clay
Low alloy steel	5-20	50-60	1-10	5-30 30-50 (6kGy/h)	5-15
Cast iron	5-20	50-60 600-700 (1 kGy/h)	5-10	-	-
Titanium	-	0.05-0.2 0.7 (10 kGy/h)	< 0.1	-	0.1

pressures. This has to be taken into account when calculating gas formation from this process in salt.

One difference most people have in mind when radiolysis in salt is discussed is the formation of aggressive gases like Cl_2 or HCl. Measurement, however, have shown that this effect can be neglected since only traces of this gases could be detected at very high integrated doses.

In conclusion differences for radiolysis in salt compared to other host rocks can be observed since

- undisturbed conditions in salt exhibit very low gas formation rates because of the lack of water,
- radiolysis may be in competition with other gas formation mechanisms in salt, and
- complex brines behave somewhat different from water.

Other mechanisms

From the remaining mechanisms for gas production microbial activity is certainly the most relevant. It is confined to organic wastes or wastes fixed in organic material like bitumen. Therefore only low and intermediate level waste forms are considered for microbial degradation. The microbes causing gas production are introduced mainly with the waste though groundwaters may contain microorganisms as well. But this is not a prerequisite for microbial gas production. For this reason it is not a decisive difference to other formations that no microbes have been found in salt formations intended for waste disposal. The limited water supply in salt will hamper microbial activity but not prevent it totally. The same is valid for the high salt concentrations in brines, which have been shown to be not a principle obstacle for microbial gas production but only reduce the number of microorganisms that may become active. So the main difference lies in the potential quantity of gas production compared to other formations.

Primary and thermal gas release from host formations is best investigated for salt. Its contribution to gas production can however be neglected compared to the other mechanisms. The amount of gas inclusions in salt lies in the range of 1 - 10 ml/kg. Similar figures have been published for crystalline rock like granite but have not been established directly on repository sites.

Calculational results

If putting together the figures for gas production mentioned up to now amounts of gas can be calculated for different host formations under comparable conditions. The emplacement of high level waste in boreholes is taken here as an example. For reason of comparison the boundary conditions like geometry, container material and dose rate were taken equal in all cases and the upper temperature limit was set at 100°C. Figure 2 gives the results for the gas production *in the first year* after emplacement. This time was chosen to evitate gas transport calculations that have to be performed site specific. The values for salt in undisturbed conditions are based on in situ measurement results and obviously the lowest. *If brine inflow* is assumed this situation is reversed since higher corrosion rates in Q brine are dominating the gas production. Assuming that convergence has reduced the free space available for brine inflow to about 5 % at the time of accidential brine intrusion balances this disadvantage already completely. This compaction can be reached within a few years and seems more representative for this scenario since brine inflow normally is not assumed during the operational phase of the repository.

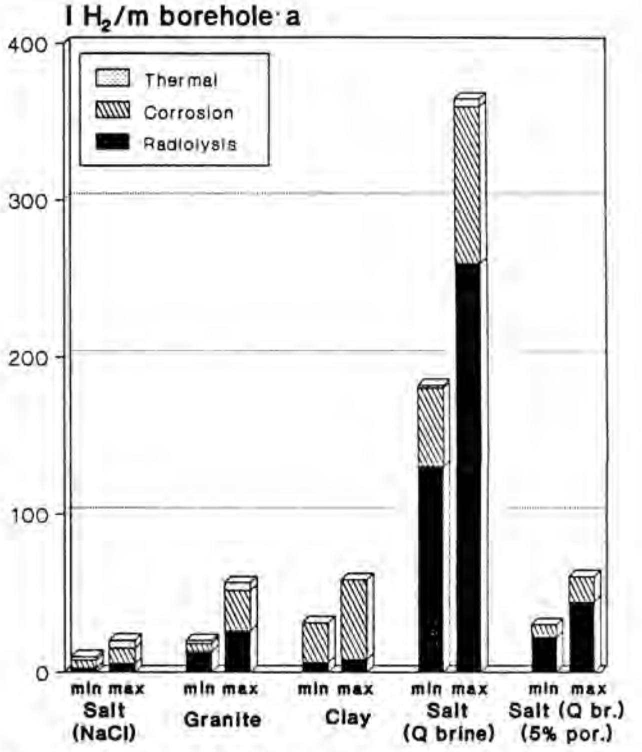

Fig. 2. Gas formation in a HLW borehole in the first year after emplacement.

GAS TRANSPORT

To assess the possible consequences of gas production the transport behavior of gas in the host formation is normally of primary interest. Therefore quite a number of codes have been developed to treat various problems in this field. Strikingly most of these applications have been performed for fissured rock while only a few were concerned with salt. Looking on the specifics of salt this turns out as easy to understand.

The problems of modelling two phase flow with moving boundary conditions and interaction with thermomechanical properties of salt has already been mentioned in general above. So far there has been only one approach up to now to put all these parameters together in one combined calculation. These calculations were performed for the WIPP site which is intended for non heat producing waste and has required a considerable effort. The still open problem for heat producing, i.e. high level waste will increase the necessary effort. Calculations for crystalline rock normally neglect these effects since the plastic properties of these formations do not allow comparable effects.

Beside this general difference gas transport in salt exhibits its specifics also in the details of modelling. The diffusion constant of gas in undisturbed salt is so low, that up to now only upper limits could be measured. Therefore gas transport by this way can be neglected. Since as mentioned above permeabilities in salt range at the lower end as well this transport mechanism too is restricted.

Figure 3 shows a sample calculation for gas transport from a borehole with high level waste in the surrounding salt

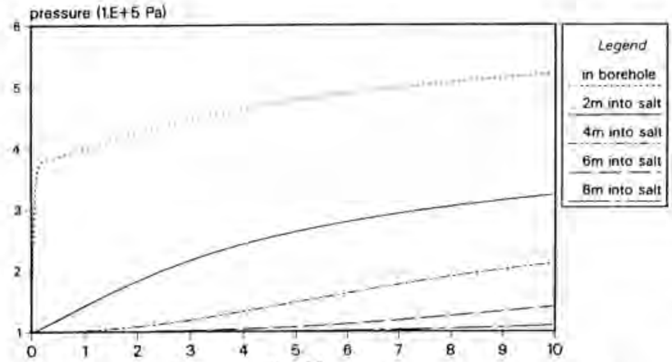

Fig. 3. Hydrogen pressure buildup and transport from a borehole.

formation. As can be seen it takes only a few meters from the borehole that gas pressures drop to nearly undisturbed values. That means gas storage as well as gas transport capacity of salt are extremely low. Modelling of gas transport in the near field of a salt repository therefore has to concentrate on engineered barriers like backfill, seals or dams. This is in strong contrast to most other formations where the transport is calculated mainly through the host rock.

In fissured rock water inflow normally is assumed instantaneously after closure of the repository for safety considerations. The transport direction follows the hydraulic gradient. Gas transport is either in the same direction in case of tight overlying formations or upwards and without coupling to the water flow. In salt as mentioned a faulted condition or accident is assumed which opens a flow path for brine intrusion. Gas transport happens along the same path. So countercurrent flow develops during the starting phase of the scenario. If all available residual volumes have been filled with brine this situation is reversed. This coupled flow behavior again is unique for salt.

In modelling gas flow from the repository Darcy's law is applied for the description of convective flow. This implies that there is no dependence of the permeability from the gas pressure. This assumption has been validated for crystalline rock or can be achieved by a mathematical correction. For salt in contrast a strong dependence of permeability from gas pressure has been found. This may be explained by assuming a Knudsen flow in salt and interaction of the gas with the grain surfaces. Experimental evidence for this explanation comes from recalculation of measured brine migration as a vapor phase in the pore space of the salt. The description as Knudsen flow worked best in reproducing the measured results.

CONCLUSION

Some essential differences between salt and other host formations in gas production and transport have been demonstrated. It was, however, not the reason for this effort to give any kind of ranking of host formations with regard to gas. This would only be possible by a very detailed site specific analysis. The intention rather was to put emphasis on the fact that comparisons of scenarios and calculational results require careful assessment of the specifics of the individual host formation and the derived repository design requirements.

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