GEOGAS IN CRYSTALLINE BEDROCK AND ITS POTENTIAL SIGNIFICANCE FOR DISPOSAL OF NUCLEAR WASTE

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ABSTRACT

In assessments of the safety of final repositories for nuclear waste situated in crystalline basement rock it is usually postulated that the transfer of radionuclides to the biosphere can take place only through transport by water. However, in order for such an assumption to be valid, it must be verified that any geogas that is present will not affect the transport - at least not to any significant degree. (The word geogas refers to the occurrence in the crystalline basement rock of substances which become gaseous at normal pressures and temperatures.)

Geogas in crystalline rock consists of species such as nitrogen, argon, helium, hydrogen, methane, carbon monoxide, carbon dioxide, hydrogen sulfide, and oxygen. The gas originates from the atmosphere, chemical reactions in the rock, the decay of radioactive elements in the rock, and degassing from the mantle of the earth. In most observed cases, geogas is dissolved in the groundwater. However, at elevated pressures and at low temperatures, methane may combine with water to form a solid phase commonly called methane-ice.

The transfer of geogas through the rock and to the surface takes place through flow in fractures. Firstly, dissolved geogas migrates due to the flow of the groundwater, and secondly, pockets of gas may form and eventually be released in the form of bursts. In the second case, the gas might act as a carrier for heavy elements through four different mechanisms: 1) formation of volatile compounds, 2) formation of surface active complexes, 3) flotation, and 4) formation of aerosols.

When a potential site for waste disposal is being evaluated, studies of geogas should form part of such a characterization programme. Favourable conditions for the formation of free gas may develop as a result of the heating of the rock by radioactive decay in the waste. It is also conceivable that methane-ice might form in the backfill of a repository in connection with a glaciation. The decomposition behaviour of such methane-ice appears to be largely unknown. Positive aspects may include the possibility of utilizing geogas flow for the non-destructive monitoring of a site after closure of the repository.

BACKGROUND AND OBJECTIVES

In assessments of the safety of final repositories for nuclear waste it is usually postulated at an early stage that any transport of radionuclides from the waste to the surface takes place through transport by water. The radioactive species are assumed either to be dissolved in the water or to appear in the form of colloids.

In order for such an assumption to be justified, it must be verified that any geogas present does not affect the transport of radionuclides to any significant degree. (In the present paper, the word *geogas* is used to mean an occurrence in crystalline bedrock of substances which become gaseous at normal pressures and temperatures.) In order for such an evaluation or verification to be performed, it is necessary that there should be a reasonable knowledge base regarding geogas and transport phenomena related to it.

The present study was prompted by this need for understanding. Thus, geological, geochemical and waste management literature has been surveyed for evidence of geogas and of transport of heavy elements by the aid of geogas¹⁻³. In particular, the following questions have been asked:

- What evidence is there regarding the existence of geogas?
- What evidence is there regarding the existence of methane-ice?
- What is the origin and composition of geogas?
- How does it move through the rock?
- What evidence is there of transport of heavy elements?
- What mechanisms might there be for such a transport?
- Is the transport of heavy elements selective?

 What conclusions can be drawn regarding the significance of geogas for the safety of a repository for nuclear waste?

With this compilation as a background, analyses have been made regarding possible mechanisms for migration and accumulation of gas as well as for transport of heavy elements.

ORIGIN

Geogas can have several origins⁴⁻⁵. Some of the gas is simply air that has dissolved in surficial water that has then infiltrated into the deeper parts of the bedrock. In this case, the geogas is expected to contain nitrogen and argon and perhaps also oxygen (if the oxygen has not already reacted with the rock and disappeared).

Another source of geogas is chemical reactions that may appear in all the parts of the rock. Thus, near the surface, cellulose or humic substances may react with dissolved oxygen, sulfate ions or iron-III to form carbon dioxide, hydrogen sulfide and methane. Other reactions may concern originally sedimentary material that is in some state of metamorphosis. Reactions may also take place between the rock and water. Another source related to chemical reactions is degassing from the mantle of the earth. Typical gases from chemical reactions are nitrogen, carbon dioxide, methane, hydrogen sulfide.

Helium-3 and hydrogen are gases that ascend from the mantle or even deeper sources. It has been reported⁶, that helium-3 is produced mainly in stellar reactions and is preserved in the mantle. Hydrogen may originate from iron hydride present in the interior of the earth.

Finally, gas is generated by the radioactive elements in the rock. Typical gases from this source are argon, helium and radon.

Sampling of geogas or water containing geogas is experimentally difficult, especially at greater depths, and we have found few complete and reliable analyses of gases from crystalline bedrock in the literature. Examples of gas composition in groundwater sampled from the crystalline bedrock at the Äspö site for the hard rock research laboratory for nuclear waste are shown in Table 1⁷. The bedrock at Äspö consists of precambrian (ca 1 700 My) granodiorites and amphibolites.

Table I. Gas concentrations (in $\mu\ell\ell\ell$) in groundwater from boreholes at Äspö. The data have been obtained by the Swedish Nuclear Fuel and Waste Management Company [7]. The calculated concentrations of different components in pure water that are in equilibrium with air are also shown for comparison.

borehole no sample depth	KLX01 272 m	KLX02 680 m	KLX01 850 m	KLX01 910 m	KAS03 129 m	KAS03 860 m	H ₂ O 20°C
N ₂ He + H ₂	25 000 88	72 000 -	55 000 6 400	37 000 3 500	20 000 -	40 000	12 000 < 0.1
CH₄ ¯	110	220	31	27	16	37	< 0.1
∞	14	1.5	0.3	0.1	11	35	-
CO ₂	-	290	620	500	1 200	175	300
O ₂	0.35	-	< 1 000	< 1 00	-	0.26	6 000

METHANE-ICE

Methane-ice is the trivial name for a solid phase that can be formed in the system methane water. It has been observed in boreholes for oil exploration in arctic regions and also in boreholes through the bottom of deep seas at all latitudes (actually along the continental shelfs)^{8,9}. Methaneice can constitute a problem in oil exploration because of its tendency to clog boreholes and thereby hinder the flow of oil and gas.¹⁰

There are two main crystallographic structures of methane-ice 11,12 . They consist of a network of hydrogen-bonded water molecules that form "cages" into which non-polar molecules such as methane may fit.

The phase diagram for methane-ice (showing the phases that can exist for different temperatures and pressures) has been established^{13,14}. It can be concluded from this diagram that methane-ice can be stable at pressures and temperatures occurring in or near a repository for spent nuclear fuel, at least if the climate is colder than at present. When, after such a cold period, the pressure is decreased and/or the temperature increased, the methane-ice decomposes to water (or ordinary ice) and (gaseous) methane. A prerequisite for such a formation (and subsequent decomposition) of methane-ice is that there must be a source for the methane.

THE FLOW PATTERN AND THE FLOW RATE OF GEOGAS

The best illustration of the flow patterns of geogas appears to come from marine geological observations^{15,16} where a clear correlation has been found between major geological fracture zones and observations of geogas. An example of this, taken from the archipelago of Stockholm, is shown in Figure 1.



Figure 1. Location of larger lineaments in the Stockholm archipelago together with the observations made of geogas eruptions. The figure has been supplied by Per Söderberg and Tom Flodén at the Department of Geology and Geochemistry at the University of Stockholm.

Figure 2. Pockmark in the Stockholm archipelago. The figure was drawn after an original in Reference [15].



A report from Finland⁵ shows that similar correlations have been found on land. The marine observations of geogas are either direct observations of bursts or of pockmarks that are formed at the sea bottom during a burst (if the bottom comprises clay or fine sand). Pockmarks appear in different sizes from decimeters to several meters. A typical pockmark is shown in Figure 2.

Large volumes of gas may be escaping when a pockmark is formed as is evidenced by the observation of pockmarks with a diameter of up to 40 meters and a depth of 2-3 meters, and of gas eruptions of up to 10 meters above sea level.

Most observations of geogas indicate that the gas appears as bursts. In boreholes, however, the observations known to the authors are only of individual, relatively small bubbles or continuous streams of bubbles. However, most analyses of water in bore holes indicate total gas pressures substantially lower than the hydrostatic pressure.

The irregularities in the flow patterns, in time as well as space, imply that it is difficult to measure or even estimate the average flow rate per unit area. Unfortunately, significant data can therefore not be provided.

TRANSPORT OF MATTER CONTAINING HEAVY METALS

Somewhat remarkable, but nevertheless, comprehensive and conclusive evidence exists^{5,17,18} which shows that matter containing heavy elements can be transported from mineralisations at considerable depths of several hundred meters and up to the surface.

In the works of Kristiansson and Malmqvist^{17,18} the heavy elements are collected on aerosol type filters mounted onto the spouts of funnels that are buried in the overburden above the crystalline bedrock. The filters are analysed for minute traces of elements by the very sensitive PIXE method (Proton Induced X-ray Emission)¹⁹.

In the Finnish study⁵, the air was sampled above the ground by sucking it through a system of filters and an absorbant solution. The solution was then analysed for various elements using an atomic absorption spectrophotometer.

With the methods used, no absolute calibration could be made. However, in several cases, differences were observed between areas that have mineralisations and those that do not.

Some examples of the results from the studies of Hämeenkylä et al⁵ and Kristiansson and Malmqvist¹⁷ are presented and compared with each other in Reference [5].

POSSIBLE MECHANISMS FOR GAS MIGRATION

The only route that has been identified as reasonably efficient for geogas flow to the surface is through major fractures in the bedrock¹. In such fractures, the geogas may either flow as a gas or as a component dissolved in the groundwater. In bedrock where the groundwater level is high - as it is in most cases in Sweden - it is likely that at least part of this transport takes place through the flow of groundwater.

The direction and velocity of the flow of groundwater is dependent on the shape of the groundwater surface, thermal conditions in the rock, differences in groundwater chemistry, tectonic effects (for instance, tidal pumping) and, probably, also the effect of geogas. In some cases, the flow may imply that the sum of the partial pressures of the dissolved gases reaches, or exceeds, the hydrostatic pressure. Thus, the condition for gas formation may be reached, either by a decrease in the hydrostatic pressure, or by an increase in temperature (or both). The critical points and curves for some geogas candidates are given in Reference¹.

An event of this nature may appear at a depth of some tens or hundreds of meters and in a fracture of perhaps 0.1 mm width, or less 20.

The formation of a gas phase in the form of a new bubble would require considerable oversaturation initially if the bubble were to develop straight out of pure water. Instead, in most cases, the initiation of a new bubble is aided by some kind of mechanism that reduces the activation energy of formation. In groundwater, this process can be expected to be facilitated by the presence of fracture and particle surfaces as well as by ionizing radiation that may be emitted from radioactive elements in the fracture coatings.

When a bubble forms, it can be expected to grow relatively rapidly in the beginning due to the oversaturation of the water in the vicinity of the bubble. The growth rate is diffusion-controlled, which implies that the rate of growth is soon slowed down. Moreover, as the bubble becomes larger, it will move upwards with increasing velocity due to the difference in density between the bubble and the water phase and in accordance with Stoke's Law²¹. Such a motion will enhance the transport of dissolved gas from the groundwater to the bubble.



Figure 3. Possible mechanisms for the growth and transport of gas bubbles in a fracture.

As the bubble grows, its diameter will eventually become comparable in magnitude to the width of the fracture. At some point, the bubble will meet a constraint in terms of a narrower portion of the rock. If it were to proceed through such a constraint, it would have to modify its shape to an energetically less favourable one. At this stage, such a change would not be expected to take place since the driving force would be too small. Instead, the bubble would be trapped.

Alternatively, the bubble was trapped even initially.

The bubble will, however, continue to grow and in doing so, expand into the fracture. When a sufficiently large pocket of gas has accumulated, a pressure will appear on the upper part of the pocket where the constraint is and force the surface to change shape. This will provide for a flow of at least a large part of the gas in the pocket through the constraint.

As it moves, the gas volume will gain momentum, expand - as the hydrostatic pressure decreases - and move to the surface at an increasing rate. Finally, it will reach the surface and become evident as a burst of gas.

The mechanisms proposed for gas migration are illustrated in Figure 3.

In boreholes, there are no constraints as described above, and the bubbles will therefore reach the surface one by one instead, as has actually been observed (cf above).

It is obvious from the description above that the flow of geogas may affect the flow of the groundwater.

POSSIBLE MECHANISMS FOR THE TRANSPORT OF HEAVY ELEMENTS BY MEANS OF GEOGAS

Four mechanisms have been identified for the transport of different elements by means of geogas:

- transport through volatile molecules that dissolve in the gas,
- transport by elements bonded to complexing agents that are surface active and enrich themselves onto the interface between the water and the gas,
- flotation (bubbles attaching themselves onto particles and lifting them) and
- transport by aerosols that may form when gas moves rapidly through a fracture in the rock.



Figure 4. Possible mechanisms for transportation of matter with geogas.

The mechanisms proposed for transport of elements by means of geogas are illustrated in Figure 4.

<u>Transport through volatile compounds that dissolve in the gas.</u> There is a large number of organometallic compounds that can be formed, many of which are volatile^{22,23}. It is also known that some elements in nature, such as mercury, cadmium, arsenic and lead, form alkylated compounds through the action of microorganisms^{4,22}. These compounds are quite volatile²² - and toxic!²⁴ - and are responsible for much of the spreading of these elements in the environment.

If - or when - such compounds are formed in the fracture systems in the rock, they may dissolve in the geogas and be transported to the surface.

<u>Surface-active complexes that are transported on the surfaces of the bubbles.</u> It is a wellknown phenomenon in surface chemistry that complexing agents may have different polar properties in different parts of their molecules²¹. Thus, in a system where bubbles are present, the energy can be lowered if the non-polar parts of such molecules direct themselves towards the gas in the bubbles.

It has been shown²⁵ that a substantial enrichment can take place on the surfaces of bubbles of air that pass through seawater. In an interesting experiment carried out in the Irish Sea,²⁵ foam and spray from such bubbles were collected and analysed for plutonium. They were found to contain 30 - 600 times more plutonium per unit volume than the sea water that they originated from.

<u>Flotation</u>. Flotation is a well-known phenomenon²⁶ that has been utilized for a long time and on a large scale in mining industry. In flotation, the specific surface energy is (naturally, or through the use of additives) higher between water and gas than between a certain mineral and gas. Thus, if the ore is crushed to a suitable size, the bubbles can lift the particles sticking onto them and leave particles of other minerals behind. It appears, that this method is particularly feasible when a separation of sulfide minerals from oxide minerals is desired.

<u>Transport by aerosols.</u> As described above, a gas pocket may release itself and move towards the surface. This motion may become rather rapid depending on the circumstances in each particular case.

The motion can be expected to depend on the width of the fracture (since the flow is likely to be limited by the viscous drag of the water making way for the gas pocket). The width of the fracture can be expected to vary in a complicated manner in each individual case. On average, however, the width is expected to increase as the distance from the surface decreases²⁰.

Furthermore, the volume of the gas increases as the hydrostatic pressure decreases during the escalation. The driving force for the gas pocket is approximately proportional to the volume of the pocket while the drag can be expected to increase considerably less rapidly or may even be relatively independent of the volume²¹.

Thus, at some stage, the motion of the gas may become sufficiently rapid in order to cause a dispersion of solid particles and/or liquid into an aerosol.

Liquid constituents in the aerosol may well evaporate as the relative humidity²¹ in the gas pocket can be expected to decrease as the hydrostatic pressure decreases. Such an evaporation of the liquid can be expected to "stabilize" the aerosol (actually make it less unstable).

POSSIBLE IMPLICATIONS FOR THE SAFETY OF A REPOSITORY FOR NUCLEAR WASTE

In the geological literature (see, for instance, Reference [27]), alterations in the composition of rock are usually explained as a result of the following:

- Weathering in combination with transport by surface waters
- Hydrothermal currents and their interactions with the rock
- Volcanism (which partly includes the flow of geogas)

Modification of the geochemistry of the earth's crust through the action of the "diffuse" flow of geogas is seldom mentioned. This is understandable in view of the very limited knowledge that exists regarding its significance. It should be remembered, however, that such an omission of this effect might - at least in certain cases - actually not be justified.

Thus, anyone attempting to assess the significance of geogas for a repository for nuclear waste can expect that the present situation of incomplete general knowledge may persist for a considerable time. It would therefore seem appropriate to consider what specific knowledge might be needed for any specific waste disposal system and site.

When a site is being characterised, studies are likely to be made of the composition of the groundwater, of the extension of the fracture system and of the water flows in these fractures. It would seem pertinent that such site characterisation studies would include careful measurements of the geogas present in the groundwater together with analyses of any influence that geogas might have on the anticipated future function of the repository.

One such influence may appear during the time when the surrounding rock has an elevated temperature due to the heat output from the waste canisters. The increase in temperature decreases the solubility of geogas in the groundwater. Thus, if the groundwater is near saturation in the nearby unheated rock, bubbles may form when such water reaches the vicinity of the canisters.

Another influence may appear in connection with a glaciation. During such an event, the temperature in the rock decreases and also the hydrostatic pressure may increase due to the weight of the ice sheet²⁸. Under such conditions, methane-ice may form in the pores of the backfill. When the climate becomes warmer, the methane-ice decomposes.²⁹ It is even conceivable that the decomposition may occur in the whole repository within a relatively limited time.²⁹ However, no records of such analyses have been found in the literature.

It should also be noted that geogas might perhaps become a positive factor in waste disposal technology. It appears to be possible that the flow of geogas could be utilized for non-destructive monitoring of the condition of the fracture system in the vicinity of the repository.

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