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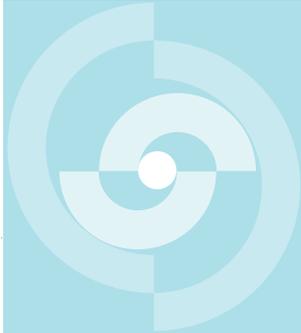
Nationale
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für die Lagerung
radioaktiver Abfälle

Cédra

Société coopérative
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pour l'entreposage
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Cisra

Società cooperativa
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TECHNICAL REPORT 85-35

Some aspects of the use of iron canisters
in deep lying repositories for nuclear waste

I. Neretnieks

February 1985

Royal Institute of Technology, Stockholm

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Le présent rapport a été préparé sur demande de la Cédra. Les opinions et conclusions présentées sont celles des auteurs et ne correspondent pas nécessairement à celles de la Cédra.

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SUMMARY

Iron canisters for high level nuclear waste embedded in compacted bentonite in deep geologic repositories will corrode forming hydrogen gas. The equilibrium pressure (when corrosion would stop) has been estimated to be between 500 and 1000 atm. under repository conditions. As this is much higher than the lithostatic pressure (weight of rock overburden) the gas must be allowed to escape before it disrupts the repository. Escape by diffusion alone is not sufficient but recent experiments (Pusch 1984) have demonstrated that the larger pores in the bentonite are blown free of water and let the gas escape before excessive pressures build up.

The potential effect of a capillary breaking layer (CBL) has been explored. A fine layer nearest the canister (e.g. quartz sand) would have much lower capillary suction pressures than the bentonite clay. Hydrogen gas formed by corrosion would drive out water from this layer. The gas/water interface would stabilize at the CBL-bentonite interface. The water cannot be driven out of the bentonite (except from the very largest pores) because of the very high suction pressures. When there is no water in contact with the iron, corrosion will slow down considerably. A steady state corrosion rate will be reached. Due to lack of data at present the steady state pressure and corrosion rate cannot be quantified but it is entirely conceivable that it will decrease by several orders of magnitude below that when water is freely available. If this occurs then an additional effect may be expected. As long as the CBL is void of liquid water no radio-nuclides can escape, even if the canister is penetrated.

ZUSAMMENFASSUNG

Der Bericht betrachtet die Korrosion von Eisenbehältern für hochradioaktive Abfälle und die damit verbundene Wasserstoffentwicklung für den Fall, dass diese Behälter in Bentonit eingebettet und in tiefen geologischen Formationen endgelagert werden. Unter solchen Bedingungen liegt der Gleichgewichtsdruck (ab welchem die Korrosionsreaktion unterbleibt) schätzungsweise zwischen 500 atm und 1'000 atm und ist somit erheblich höher als der Gebirgsdruck. Deshalb muss das Gas entweichen können, da sonst das Gefüge des Wirtgesteins durch den Gasdruck verändert werden könnte. Ein Entweichen durch Diffusion allein reicht nicht aus, jedoch haben neuere Experimente (Pusch 1984) gezeigt, dass die grösseren Poren des Bentonits durch den Gasdruck von Wasser befreit werden, und dass somit das Gas entweichen kann, bevor unzulässig hohe Drücke aufgebaut werden.

Die mutmassliche Wirkung einer Kapillarbarriere (CBL) wird untersucht. Eine dünne Schicht z.B. aus Quarzsand um den Behälter würde eine viel kleinere Kapillarsaugspannung aufweisen als der Bentonitton. Durch Korrosion entstehendes Wasserstoffgas würde Wasser aus dieser Schicht verdrängen, sodass sich der Uebergang Gas/Wasser an der Grenze CBL/Bentonit stabilisiert. Wegen der sehr hohen Saugspannungen kann das Wasser nur aus den grössten Poren des Bentonits verdrängt werden. Sobald kein Wasser mit dem Eisen in Kontakt steht, wird die Korrosion beträchtlich verlangsamt. Eine stationäre Korrosionsrate wird erreicht. Mangels Daten können weder der stationäre Druck noch die stationäre Korrosionsrate quantifiziert werden. Es ist jedoch durchaus zu erwarten, dass Korrosionsrate und Druck um Grössenordnungen reduziert werden gegenüber dem Fall des unbegrenzt verfügbaren Wassers. Ueberdies ist ein zusätzlicher Effekt zu erwarten. Solange die CBL frei von Wasser bleibt, können keine Radionuklide entweichen, auch wenn der Behälter undicht wird.

RESUME

L'on considère la corrosion de conteneurs de fer pour déchets hautement radioactifs ainsi que l'évolution d'hydrogène qui en résulte dans le cas où le conteneur est enrobé dans de la bentonite et stocké définitivement dans un dépôt géologique profond. Dans ces conditions la pression d'équilibre (à partir de laquelle la corrosion est arrêtée) est estimée se situer entre 500 atm et 1'000 atm, ce qui est nettement plus élevé que la pression lithostatique. En conséquence il est nécessaire d'assurer la possibilité au gaz d'échapper, faute de quoi il risque de modifier la structure de la roche d'accueil. La diffusion seule ne suffit pas à assurer le transport du gaz, cependant des expériences récentes (Pusch 1984) ont démontré que les pores de grandes dimensions se vident de leur eau sous l'influence de la pression du gaz et qu'ainsi le gaz peut s'échapper avant que la pression atteigne des valeurs inadmissibles.

On a étudié l'effet potentiel d'une barrière capillaire (CBL). Une couche mince, par exemple de sable de quartz, entre le conteneur et la bentonite, aurait une tension de succion capillaire beaucoup plus faible que celle de la bentonite. L'hydrogène formé par la corrosion repousserait l'eau de cette couche. La transition eau/gaz se fixerait à la zone de contact CBL/bentonite. L'eau ne saurait être expulsé de la bentonite (à l'exception de quelques pores de très grandes dimensions) du fait des tensions capillaires élevées. Du moment que l'eau n'est plus en contact avec le fer, la corrosion sera considérablement ralentie. Un taux de corrosion stationnaire s'établira. On manque présentement de données et conséquemment l'on ne peut donner des valeurs précises pour la pression et le taux de corrosion en régime stationnaire. Il est néanmoins parfaitement concevable que le taux de corrosion soit plus petit de plusieurs puissances de dix que lorsque l'eau est disponible en quantité illimitée. Si cela est bien le cas, l'on peut s'attendre à un effet supplémentaire: aussi longtemps que le CBL ne contient pas d'eau, aucun radionucléide ne saurait s'échapper, même si le conteneur a perdu son étanchéité.

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1 BACKGROUND

For high level waste (HLW) repositories, iron is considered in several countries as a candidate material for the canisters which will contain the HLW or spent fuel. For the HLW repositories, the iron canisters might be surrounded by a low permeability backfill such as compacted bentonite clay (KBS-3 1983, NAGRA-Gewähr 1985).

In the above mentioned cases, the repositories are located deep underground (500-1300m), below the water table and the iron will eventually be wetted by the water seeping in through the bentonite clay. The iron will corrode by reaction with dissolved oxygen (if available - in deep locations the waters are reducing) and with water. In the latter case hydrogen gas will form and must escape. It can escape by diffusion in the water filled pores or by flow through the larger pores of the porous material. Water will simultaneously be drawn in by capillary forces and by flow in the initial stages where there is a pressure gradient towards the canister. If the hydrogen production is large, considerable pressures can build up as the hydraulic conductivity and diffusivity of bentonite is low.

The hydrostatic pressures are expected to be 50-130 bars at the depths considered. The rock stresses may be very much larger (150-250 bar in Sweden at 500 m depth). In Switzerland up to 350 bar rock stresses are expected at 1300 m. The rock may thus contain a body with much higher internal overpressure than the hydrostatic pressure. There are several questions to be approached:

1. Can the gas pressure reach such values that it will exceed the confining stress of the surrounding rock?
2. Can the hydrogen pressure reach such levels that corrosion no longer can take place due to thermodynamic reasons?
3. Can the porous structure of the clay materials decrease the activity of water in the two phase flow situation where so high capillary pressures develop that this will influence (lessen) the corrosion of the iron?

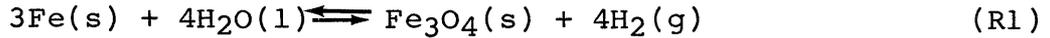
After an initial period where the entrapped oxygen reacts with the iron, the reaction will be between iron and water. Only these reactions will be considered below.

2 BENTONITE PROPERTIES

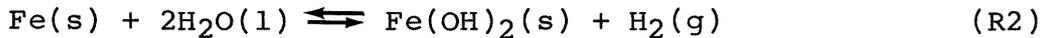
The bentonite clays considered consist of more than 80% smectite minerals which exist in the form of very thin crystals. In the compacted state which will exist in the repositories (wet density ca. 2000-2100 kg/m³) the average crystal distances are 15-20 Å. Because there are crystal agglomerates and foreign material with larger size, larger pores and voids are present. Water in the intercrystalline layer is very strongly bound by adsorption (Kahr et al. 1984). Up to 25-30 % by weight of water can be adsorbed strongly. Additional water will increasingly be looser bound in the material. At a compaction degree equivalent to a wet density of 2000 kg/m³, the clays have a swelling pressure of the order of hundreds of atm. It varies somewhat with the source of the bentonite. Lower densities give lower swelling pressures (Pusch 1980 TR 83-13, Kahr et al. 1984). Adsorption isotherms and energies as well as the activity of water in bentonite clays, have been measured (Kahr et al. 1984). Hydraulic conductivities of water saturated clay with different degrees of compaction have been measured by Pusch 1980 (KBS TR 80-16) as well as gas transport rates through compacted bentonite (Pusch 1983, Pusch 1984, Neretnieks and Skagius 1978). Gases dissolved in water may diffuse through a compacted bentonite layer and gas may also flow through the larger pores, provided sufficient pressure difference is imposed to overcome the capillary (and adsorption) forces in these pores. Figure 1 shows a conceptual picture of a bentonite barrier.

3 THERMODYNAMIC CONSIDERATIONS

In anoxic waters the two most probable iron corrosion products are magnetite and ferrous hydroxide. The reactions can be written



and



The equilibrium constants can be written for R1

$$K_1^4 = \frac{f_{\text{H}_2}^4 \cdot a_{\text{Fe}_3\text{O}_4}}{a_{\text{H}_2\text{O}}^4 \cdot a_{\text{Fe}}^3} = \frac{\phi_{\text{H}_2}^4 P_{\text{H}_2}^4 \cdot a_{\text{Fe}_3\text{O}_4}}{a_{\text{H}_2\text{O}}^4 \cdot a_{\text{Fe}}^3} \quad (1)$$

and for R2

$$K_2 = \frac{f_{\text{H}_2} \cdot a_{\text{Fe(OH)}_2}}{a_{\text{H}_2\text{O}}^2 \cdot a_{\text{Fe}}} = \frac{\phi_{\text{H}_2} P_{\text{H}_2} \cdot a_{\text{Fe(OH)}_2}}{a_{\text{H}_2\text{O}}^2 \cdot a_{\text{Fe}}} \quad (2)$$

f and ϕ denote fugacity and fugacity coefficient respectively, a denotes activity.

For 25°C, 1 atm and activity of water, iron and corrosion products equal to 1, the equilibrium fugacity of hydrogen is between 630 and 705 atm for the magnetite reaction and between 50 and 160 atm for the ferrous hydroxide reaction. The magnetite reaction thus is the more probable from thermodynamic considerations at the assumed temperature and pressure. The fugacity coefficient at fugacities of 600 - 700 atm is around 1.3 - 1.4 (see below). If the water activity is 1 then about 400 atm equilibrium pressure would be expected for the magnetite reaction.

This pressure is so high that the pressure influence on the equilibrium must be assessed. Furthermore the influence of elevated temperature must be investigated because the waste gives off heat causing the temperature in the repository to rise by 50-100°C depending on the layout of the repository and the age and concentration of the waste (or spent fuel).

3.1 Influence of temperature

The temperature influence can be assessed if the enthalpy of reaction ΔH_r is known

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = -\frac{\Delta H_r}{RT} \quad (3)$$

As ΔH_r is reasonably independent over the temperature range of interest, integration of (3) with $\Delta H_r = \Delta H_r^0$ gives

$$\ln(K_{T2}/K_{T1}) = -\frac{\Delta H_r}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (4)$$

R is the gas constant and T is the absolute temperature.

For $T_2 - T_1 = 55K$ (at $T_2 = 353K$) $K_{353} = 1.52$ to 1.59 times K_{298} (for the two different data in table 1). Expressed in fugacity this gives 958 to 1086 atm. Accounting for the fugacity coefficient the equilibrium pressure will be on the order of 600 atm at $80^\circ C$.

3.2 Influence of pressure

The influence of pressure may be assessed by the relation

$$\left(\frac{\partial \ln a_i}{\partial P}\right)_T = V^0/RT \quad (5)$$

or

$$a_i^P = a_i^1 \cdot e^{V^0(P-1)/RT} \quad (6)$$

where V^0 is the mole volume of the components. If the pressure were equal for all components equation (6) could be used directly to modify K. In the case where a mechanical stress exists between the porous clay and the iron canister and capillary or osmotic effects play a role this is not necessarily the case. The canister and corrosion products are subject to the mechanical swelling pressure P_M of the clay at the points of contact, whereas the water in the larger pores is at the hydrostatic pressure P_H . Figure 2a shows this case. When and if the hydrogen production rate becomes so high that hydrogen cannot escape at the

same rate as it is produced, gas may form. (It will be shown later that the diffusion rate is not large enough at estimated corrosion rates to carry all gas away.) The gas pressure P_G will be larger than the hydrostatic by P_C -the capillary pressure in the pores.

$$P_G = P_H + P_C \quad (7)$$

The corrosion products will (at least locally where further corrosion takes place) be subject to the gas pressure. This may vary between slightly above the hydrostatic pressure P_H and up to the lithostatic stress (pressure) P_L . At 1300 m depth (Nagra concept) $P_H = 130$ atm and P_L approx. 350 atm. If the gas cannot escape fast enough, P_M may increase from the swelling pressure to at most the lithostatic pressure P_L . The bentonite might then be compacted and leave a gas volume around the upper part of the canister.

If the larger pores open up before this happens and have a sufficient transport capacity to let the gas escape by flow, the pressure build up will reach a stationary value, lower than if gas must escape by diffusion only.

3.3 The influence of pressure on the activities

For a system pressure of P_G this acts on the gas and the two solids whereas the water is at hydrostatic pressure P_H (this is explained and described under "Capillary effects").

Thus at system pressure P_G the fugacity of the hydrogen gas may be derived from equation (1) and the above relations:

$$f_{H_2} = K_T a_{Fe}^{3/4} \cdot a_{H_2O} / a_{Fe_3O_4}^{1/4} \quad (8)$$

where

$$a_{Fe} = e^{V_{Fe}(P_G-1)/RT} \quad (9)$$

$$a_{Fe_3O_4} = e^{V_{Fe_3O_4}(P_G-1)/RT} \quad (10)$$

$$a_{H_2O} = e^{V_{H_2O}(P_H-1)/RT} \quad (11)$$

K_T is the equilibrium constant at $P = 1$ atm and temperature T . Here the influence of capillarity has been accounted directly by having the water activity at P_H instead of at system pressure.

Combining equations (8) to (11)

$$f_{H_2} = P_G \cdot \phi_{H_2O} = K_T \cdot e^{\frac{3/4 V_{Fe}(P_G-1)}{RT}} \cdot e^{\frac{V_{H_2O}(P_H-1)}{RT}} \cdot e^{-\frac{1/4 V_{Fe_3O_4}(P_G-1)}{RT}} \quad (12)$$

P_G may be solved for if the pressure relation of ϕ is known. This will be obtained below.

3.4 The fugacity of hydrogen gas

Fugacity can be seen as the "would be pressure" if the gas were ideal. As it is not at higher pressures, a correction is needed. The real pressure P may be related to the fugacity by a fugacity coefficient

$$f = \phi P \quad (13)$$

This may be obtained via the compressibility of a real gas z by

$$\frac{\partial \ln \phi}{\partial P} = (z - 1)/P \quad (14)$$

For hydrogen $z = 1 + 5.4 \cdot 10^{-4}P$ (P in atm) (Perry and Chilton, 1973, Table 3-163) in the range $P = 0-100$ atm for 80°C and ϕ is obtained to be

$$\phi = e^{5.4 \cdot 10^{-4}P} \quad (15)$$

Equation (15) yields

P (atm)	ϕ
100	1.054
200	1.11
300	1.18
400	1.24

3.5 Capillary effects

The pressure of the water outside the bentonite is $P_H = 130$ atm. In the bentonite at the bentonite-gas interface it is equal to the gas pressure at that point P_G . This is on the average equal to the swelling pressure throughout the bentonite because it is compacted due to the external pressure and as it is plastic the pressure will be equal throughout. The activity of the water in the pore at the meniscus will then be the same as that of water at pressure P_H because the pore water is in equilibrium with the water in the rock.

Compared to reference pressure P_G at which the activities for the solid components were calculated the activity of the water will change (decrease) because of a pressure decrease from P_G to P_H . To quantify the effect of the capillary forces the decrease in activity can be assessed by equation (6).

$$RT \ln a_{P_G} / a_{P_H} = V_{H_2O} (P_G - P_H) \quad (16)$$

Compared to if the water were at pressure P_G the decrease in activity when it is at P_H is

$$a_{P_H} / a_{P_G} = e^{-V_{H_2O}(P_G - P_H)/RT} = e^{-6.22 \cdot 10^{-4}(P_G - P_H)} \quad (17)$$

with $P_H = 130$ atm and $V_{H_2O} = 18.02 \text{ cm}^3/\text{mol}$, $T = 353^\circ\text{K}$ we obtain

P_G	a_{P_H} / a_{P_G}
130	1
200	0.96
300	0.90
400	0.85

In equations (11) and (12) the activity above 1 atm was calculated instead of the activity below P_G . The treatments lead to identical results as instead of going from $P = 1$ to $P = P_G$ and then down from P_G to P_H we go directly from $P = 1$ to P_H in equation (11). The equations (16) and (17) were introduced for illustration purposes and future reference.

3.6 Equilibrium pressure of hydrogen

Combining equations (1), (4), (12) and (15) we obtain for $t = 80^\circ$ and the data in Table 2

$$P_G = 700 \cdot 1.54 \cdot e^{1.84 \cdot 10^{-4}(P_G-1)} \cdot e^{6.22 \cdot 10^{-4}(P_H-1)} \cdot e^{-3.84 \cdot 10^{-4}(P_G-1)} \cdot e^{-5.4 \cdot 10^{-4}(P_G-1)} \quad (18)$$

solving for P_G gives

$$P_G = 699 \text{ atm at } t = 80^\circ\text{C}$$

For some other temperatures the equilibrium pressure is

516 atm	25°C
618 atm	55°C
819 atm	120°C

The variability of the data is considerable and the predicted equilibrium pressures may well be in error by several tens of %. The equilibrium pressures will be well in excess of the lithostatic pressure and thus cannot be permitted.

4 ESCAPE OF HYDROGEN

The hydrogen which evolves by corrosion may escape by diffusion through the backfill and if this transport rate is not sufficient, flow will eventually take place. If the escape rate by these mechanisms is not sufficient to let the pressure stay below the lithostatic pressure, the rock will expand and the repository may be disrupted. Diffusivities in compacted fully water saturated bentonite have been measured by Neretnieks and Skagius (1978) and Eriksen and Jakobsson (1982). An experiment by Pusch (1983) may also be used to evaluate diffusivities of dissolved gas through bentonite. Experiments have recently been performed to investigate how gas may flow through a compacted initially water saturated bentonite layer (Pusch 1984).

The diffusivity for H_2 (aq) in bentonite was found to be $0.4 - 3 \cdot 10^{-11} \text{ m}^2/\text{s}$ in the different investigations. The highest value was obtained in Pusch's experiment where the pressure was kept at 90-100 atm. The other two experiments were performed at 1 atm and gave $0.4 \cdot 10^{-11} \text{ m}^2/\text{s}$ (Eriksen and Jakobsson 1982) and $1.8 \cdot 10^{-11} \text{ m}^2/\text{s}$ (Neretnieks and Skagius 1978). The differences may in part at least be due to differences in compaction of the bentonite.

4.1 Escape by diffusion

Fick's first law may be used to estimate the rate of escape by diffusion of the dissolved hydrogen

$$N = -D_{H_2} A \frac{dc}{dz} \quad (19)$$

The relation between the concentration C and the hydrogen pressure can be expressed by a linear relation - Henrys law for low and intermediate pressures.

$$P = H \cdot X = H \cdot C / C_0 \quad (20)$$

within the pressure range of interest the errors involved are less than a factor 2. H is Henrys constant, X is the mole fraction hydrogen in solution and C_0 is the molar concentration of the mixture (practically only water). $H = 6 \cdot 10^4 \text{ atm}$ (Perry) for $t < 100^\circ\text{C}$ and $H/C_0 = 1.5 \cdot 10^3$. The hydrogen concentration at 130 atm pressure is 0.087 kmol/m^3 .

The transport area A and barrier thickness Z can be estimated from the geometry of the tunnel. The canister is 2 m long with a diameter of 0.96m. The tunnel has a diameter of 3.7 m. Including the ends of the canister $A = 8\text{m}^2$ at the canister surface. The thickness of the bentonite is

approx. 1.3 m radially. Because of the cylindrical symmetry and ever expanding A with Z we use $A = 10\text{m}^2$. With $D = 10^{-11} \text{ m}^2/\text{s}$, $N = 10^{-11} \cdot 10 \cdot 0.087/1.3 = 6.7 \cdot 10^{-12} \text{ kmol/s}$ = $2.1 \cdot 10^{-4} \text{ kmol/year}$.

With reaction R1 this is equivalent to $1.58 \cdot 10^{-4} \text{ kmol/year}$ iron corroded. This is 8.9 g iron per year which has produced hydrogen by reaction with the water. The variability of data leaves an uncertainty in the results of a factor 5 up or down. It may thus be expected that the hydrogen that evolves by corrosion of between 2 and 50 g/year iron may escape by diffusion.

2 g/y is equivalent to an average corrosion depth of $0.032 \text{ }\mu\text{m}$ and 50 g/y gives $0.8 \text{ }\mu\text{m/year}$ iron corroded. This is far below the expected corrosion rate which has been estimated to be on the order of tens of $\mu\text{m/year}$. Even assuming that the hydrogen pressure would increase to the lithostatic pressure ca. 350 atm, this would still not be enough to let the hydrogen diffuse out.

The increasing hydrogen pressure will probably decrease the rate of corrosion because the reaction will have to take place nearer the equilibrium pressure, but assuming that the reaction rate is proportional to the difference between the equilibrium pressure and the existing pressure, this would give a maximum of a factor 2 decrease in reaction rate.

With the data available at present the production rate of hydrogen by corrosion may be considerably larger than the escape rate by diffusion. If there were no other escape mechanisms the pressure would try to increase towards several hundreds of atmospheres above the lithostatic pressure.

4.2 Escape by flow

Pusch (1984) has recently performed experiments to determine at which pressure differences the water in the pores of the bentonite will be blown out and thus when gas transport by flow can start. In the experiments the gas flow conductivity was also determined. The results can be summarized as follows: at an overpressure (differential pressures) of 20-90% of the swelling pressure of the bentonite, flow starts to take place. The transport capacity rapidly increases from that due to diffusion by a factor of 100-1000.

This applies for swelling pressures between 18 and 450 atm. At the higher swelling pressures the overpressure needed was found to be nearer to the swelling pressure. At very low initial swelling pressures (wet densities approx.

1700-1900 kg/m³) the flow started at differential pressures about equal to or even larger than the initial swelling pressure. In two of these experiments there was a pressure on the low pressure side of 28-34 atm. Because of the gas pressure acting on the inflow side of the sample (60 and 92 atm respectively), it must have been compacted and caused a swelling pressure at least equal to the pressure difference. The breakthrough pressure is then at most 23 to 62 % of the real swelling pressure. There is at present data only from a few experiments. The critical differential pressure for gas breakthrough by flow may be anywhere between a few 10s of % and up to 90 % of the actual swelling pressure.

It will be examined below what a compaction of the clay by the gas pressure may lead to. At this stage it is assumed that the gas pressure, when it becomes larger than the original swelling pressure, will compact the bentonite and increase its swelling pressure until the latter becomes equal to the gas pressure. The two opposing forces are then in balance, as shown in Fig. 3.

If the critical breakthrough pressure is 20 % of the swelling pressure, then for a swelling pressure $P_M = 160$ atm, 32 atm would suffice for flow to begin. The gas pressure would then be $P_H + 32 = 162$ atm. This is in practice equal to the swelling pressure. The pressures are then equal and the bentonite needs not to be compacted or try to expand by swelling.

The swelling pressure P_M may be larger than the gas pressure P_G because of mechanical stresses. It may also become equal to P_G . The gas pressure at the high pressure side acting on the bentonite will compact the bentonite and become equal to the swelling pressure, the swelling pressure P_M becomes (The pressure difference $P_G - P_H$ is a fraction of the swelling pressure at breakthrough $f_r \cdot P_M$. As $P_M = P_G$ in this case, $P_M - P_H = f_r \cdot P_M$):

$$P_G = P_M = P_H / (1 - f_r) \quad (21)$$

Here f_r is the fraction of the swelling pressure at which flow starts. The Table below gives the swelling pressure P_M for different fractions f_r when the hydrostatic pressure $P_H = 130$ atm.

The swelling pressure and gas pressure that would build up before flow starts for different critical breakthrough pressure fractions f_r is:

f_r	$P_M = P_G$ atm
0.2	163
0.3	186
0.4	217
0.5	260
0.6	325 Lithostatic pressure
0.7	433
0.8	650
0.9	(1300) larger than equilibrium pressure

With the above assumption it is not obvious if the critical breakthrough pressure will be reached before the lithostatic pressure is exceeded.

The assumption that the swelling pressure P_M is equal to or larger than the gas pressure disregards the impact on the force balance of the hydraulic pressure P_H . Under certain assumptions the gas pressure under non-flow conditions would be equal to the sum of the swelling pressure and the hydraulic pressure. This implies that there would be no compaction of the clay under non-flow conditions as long as the critical gas breakthrough pressure is less than the swelling pressure. The experimental evidence available at present is not sufficient to fully clear this matter.

5 CAPILLARY TRANSPORT OF WATER

The corrosion rate might be decreased if it were possible to limit the availability of water to the iron surface. The transport rate of water in the clay, although very low, is sufficient to transport the equivalent amount of water to corrode iron at the rate discussed above. The water will move very readily, driven by capillary forces in the smaller water filled pores, even if there is flow of gas outward in the larger pores. The smaller pores and intercrystalline voids have a considerable capillary suction capacity. For round pores or slits it can be determined from

$$P_C = 2 \gamma / r_0 \quad \text{circular pore} \quad (22a)$$

$$P_C = 2 \gamma / \delta \quad \text{infinite slit} \quad (22b)$$

γ is the surface tension of water, r_0 the tube radius and δ the width of the slit.

The activity of the water in the slit or pore at a given capillary (suction) pressure can be determined from equation (6) considering the fact that the pressure decreases from the gas side of the meniscus to the water side.

$$a_c = e^{-V_O P_C / RT} \quad (6)$$

In this context it is also called the Kelvin equation (Adamson 1982 p.54).

Table 3 gives the activity of water and the suction pressure for different r_0 or δ calculated for a surface tension $\gamma = 0.072$ N/m which is valid for ambient temperature. The capillary pressures are also directly related (on average for a pure bentonite crystal system) to the swelling pressure of the bentonite. The swelling pressure is the pressure which acts on the water in the compacted bentonite. The water in the confined bentonite is (or was) in contact with an unconfined water mass outside the confined bentonite body at pressure $P_H = 1$ atm (as often is the case in laboratory determination of the swelling pressure). The water in the bentonite when subject to the swelling pressure has the same activity as the water outside at pressure 1. If the swelling pressure were released but no more water added, the activity of the capillary and adsorbed water would be less than 1 by the amount given by equation (6) with the swelling pressure P_M instead of P_C . In practice the swelling pressure is less than what would be expected from measurements on average crystal distances (Kahr et al. 1984).

To expell water by flow from a compacted bentonite one would expect to need a pressure higher than the capillary pressure in the pores. As the pore sizes are not equal, the larger pores with the smaller capillary pressures will be emptied first. This has been experimentally observed by Pusch (1984).

5.1 Corrosion rate

The corrosion rate of iron in anoxic water has been estimated to be on the order of 10-20 $\mu\text{m}/\text{year}$ or less (Grauer 1984). It is expected that the magnetite layers will form protective layers which will decrease the rate of corrosion (Heitz 1984, Heusler 1984) but as it has not been demonstrated to do so under repository conditions it seems prudent to assume that the protective layers do not decrease the average corrosion rate to well below 1 $\mu\text{m}/\text{year}$. It is known that for iron corrosion to take place there must be an electrolyte in contact with the iron (Mattsson 1984, Grauer 1984b). The capillary forces in the small pores in the bentonite will pull in water to the canister to replenish that water which has reacted. If the liquid water could be kept away from the canister surface, the iron would not corrode. This idea will be explored below.

6 CAPILLARY BREAKING LAYER

If liquid water were not present to form an electrolyte in contact with the iron, corrosion would not take place (Mattsson 1984, Grauer 1984b). Liquid water can be hindered from flowing into the iron if a Capillary Breaking Layer (CBL) is inserted between the canister and the bentonite. A capillary breaking layer may consist of a porous material which has a much larger pore size than the bentonite clay. If there then is a gas overpressure (formed by corrosion) $P_G = P_H + P_C$, the pores within the CBL which have a capillary suction pressure $P_{CBL} < P_C$ will be empty because they cannot draw the water in against the gas pressure P_G . Figures 3 and 4 illustrate this effect. The water-gas interface is in the larger pores of the bentonite which have the pore size just giving rise to a capillary pressure P_C . Thus as long as there is an overpressure there will be no water near the canister. The small pores of bentonite will not release the water to the CBL.

6.1 Impact on corrosion

It must be expected that the corrosion products of the iron are porous and that they at least in some places form very fine pores. In the pores which are smaller than those in the bentonite which contain gas, a liquid water phase may form by capillary condensation. The activity of that water will be slightly less than that in the bentonite, because a driving force (activity difference) is needed to transport it from the bentonite to the canister wall. The transport can take place by diffusion in the gas phase and possibly by surface diffusion on the surfaces of the CBL particles. Furthermore the temperature at the canister surface is somewhat higher than the surrounding, because of heat produced by the radioactive decay of the waste in the canisters. This will also lead to a decrease in the size of the pores where liquid water might form due to capillary condensation. The relative humidity at the canister surface related to the water vapor pressure at the capillary pore opening in the bentonite will be less than 1 due to the above mentioned effects. At lower relative humidities corrosion slows down and at relative humidities less than about 60% iron corrodes at extremely slow rates even in an oxygen-rich atmosphere. This effect is utilized to stop corrosion by having a low humidity atmosphere where iron objects are kept. The decrease in relative humidity for a given vapor pressure by an increase in the temperature is about 5 % units for 1°C in the temperature range 25°C - 100°C.

The long term temperature gradients near the canister are expected to be less than 1°C per m. The temperature effect is thus not expected to be large.

There are however several effects working in the same direction. The increased hydrogen gas pressure will tend to decrease the corrosion rate, the capillary breaking layer in the bentonite with the canister and the slight temperature gradient will further decrease the driving force for the chemical reaction. The pore sizes of the magnetite will be considerably larger than those of the bentonite (on average).

At present these effects cannot be quantified due to lack of data but it seems quite conceivable that they combined will lead to a steady state pressure well below the litho-static pressure.

If the pressure levels off at levels above the hydrostatic pressure but below the gas breakthrough pressure, the hydrogen will escape by diffusion only. In that case the corrosion rate can directly be assessed by the escape rate of the hydrogen. This was previously estimated to be between 0.03 and 0.8 $\mu\text{m}/\text{year}$ (2-50 g/year). This low corrosion rate would make the iron in the canister last 0.2 - $5 \cdot 10^6$ years although penetration might occur sooner due to mechanical failure.

6.2 Initial phase with water intrusion

During the initial phase when there is still oxygen in the backfill, the iron will corrode by reaction with oxygen. No hydrogen forms during this phase. The nitrogen in the air will dissolve in the intruding water in the backfill as the pressure increases. The gas pressure will however increase and the water will have to move against increasing pressure. The CBL will not start functioning until the gas pressure there is larger than the hydrostatic pressure. As this will not be reached before the gas volume has decreased to less than $1/P_H$ (1/130) if no hydrogen evolves, the CBL must be expected to be intruded by water during this phase. As the corrosion starts and hydrogen evolves, the pressure starts to rise. Water will begin to flow outward driven by the hydrogen gas pressure when it becomes larger than P_H (130 atm). If the hydraulic conductivity were very low, the water might not have time to be driven out before the pressure reaches unacceptable levels (P_L). The pressure needed to expell the water at the same rate as hydrogen is formed by corrosion is investigated below.

The water flow rate is:

$$N_W = K_P A i = K_P A \frac{(P_G - P_H)}{\rho_{H_2O} g \Delta Z} \quad m^3/s \quad (23)$$

The production of hydrogen gas by corrosion is:

$$\dot{n}_{H_2} = \frac{4}{3} \dot{n}_{Fe} = \frac{4}{3} \frac{r_{corr} A \rho_{Fe}}{M_{Fe}} \quad kmol/s \quad (24)$$

and the resulting gas production rate (in m^3/s) compressed at P_G is:

$$N_{H_2} = \dot{n}_{H_2} \frac{RT}{P_G} \quad m^3/s \quad (25)$$

K_P	hydraulic conductivity
A	area through which flow takes place (taken to be the same as the surface of the canister)
i	hydraulic gradient
g	gravitational constant
\dot{n}_{H_2}	rate of production of hydrogen by corrosion
n_{Fe}	rate of corrosion
r_{corr}	velocity of corrosion (m/s)
ΔZ	thickness of the bentonite

The pressure at which the water flow rate out is the same at which gas is produced is obtained by equating equations (23) and (25):

$$P_G(P_G - P_H) = \frac{4}{3} \frac{RT \rho_{Fe} r_{corr} \Delta Z \rho_{H_2O} g}{M_{Fe} K_P} \quad (26)$$

with $R = 8200 \text{ m}^3 \cdot \text{Pa} / \text{kmol} \cdot \text{K}$, $T = 353 \text{ K}$, $\rho_{\text{Fe}} = 7800 \text{ kg} / \text{m}^3$,
 $\Delta Z = 1 \text{ m}$, $\rho_{\text{H}_2\text{O}} = 1000 \text{ kg} / \text{m}^3$, $g = 9.81 \text{ m} / \text{s}^2$, $M_{\text{Fe}} = 55.85$
 $r_{\text{corr}} = 30 \text{ } \mu\text{m} / \text{year}$ we obtain for

$$\begin{array}{ll} K_p = 10^{-13} \text{ m} / \text{s} & P_G = 165 \text{ atm} \\ K_p = 10^{-14} \text{ m} / \text{s} & P_G = 297 \text{ atm} \end{array}$$

Even for the highest reasonable corrosion rate combined with the lowest hydraulic conductivity that might be expected, ($K_p = 10^{-14} \text{ m} / \text{s}$) the water can be expelled at pressures below the lithostatic pressure.

6.3 Impact on the escape of radionuclides

During the period when there is no liquid water in the capillary breaking layer the radionuclides which have no or very low vapor pressures will have no liquid water in which to migrate from the canister. This applies to practically all species of interest in nuclear waste. There will be some water adsorbed on the surfaces on the CBL but there are many candidate materials available that have very small sorption capacities of water i.e. quartz sand. In such materials the transport capacity for dissolved nuclides will be very small due to the low amount of water as well as due to the small surface of the CBL. This has been chosen with particle sizes so large (i.e. $d_p = 0.5 \text{ mm}$) that the capillary forces are negligible compared to the capillary forces in the bentonite. The specific surface of a sand with particle diameter 0.5 mm will be about 10^6 times smaller than that of the bentonite. The amount of water would then be smaller by about the same amount or more, as the water sorbed on the grains is one or a few molecular layers thick only. The transport rate of nuclides in the absorbed layer of water would then become negligible if by no other reason than due to the lack of water.

As long as there is no liquid water present in the CBL, radionuclide transport will in practice be negligible.

7 DISCUSSION AND CONCLUSION

The thermodynamic data on iron corrosion by water reaction to form magnetite indicate that equilibrium pressures up to nearly 1000 atm might be expected. The small inaccuracies in the data have quite strong effects on the equilibrium pressure. It may very well be considerably lower. The other potential corrosion product - ferrous hydroxide - would have considerably lower equilibrium pressure, but it would tend to transform to magnetite and as the rates are not known, it must at present be assumed that the magnetite reaction would determine the pressure.

The projected corrosion rates produce hydrogen at a rate much higher than what can escape by diffusion. Recent gas flow measurements in compacted bentonite indicate that hydrogen may escape by flow with overpressures less than the lithostatic pressure.

The introduction of a capillary breaking layer may considerably slow down the corrosion because it would not allow the water to come in direct contact with the iron. The water would have to be transported to the iron by mainly gas diffusion and must condense in capillaries finer than those from where it evaporated in the clay. Hygroscopic effects may also cause the water to condense at the iron surface.

The lack of experimental data does not allow these effects to be quantified at present. If it could be shown to work as projected, the canister life time might be prolonged by several orders of magnitudes and even after failure of the canister no radionuclide release could take place as long as a sufficient corrosion rate is kept up to keep the capillary breaking layer dry.

8

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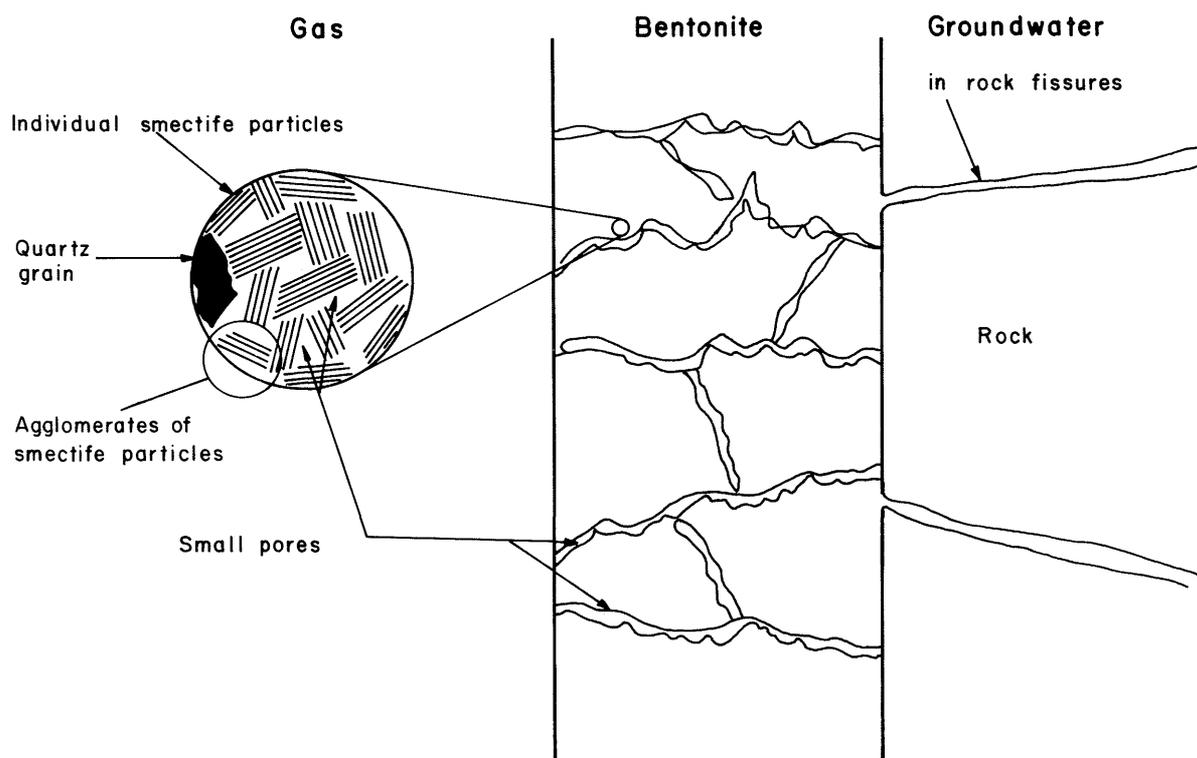


Figure 1: A compacted bentonite barrier may contain pores in addition to the voids between the individual smectite particles. Natural bentonites also contain a minor fraction of other minerals.

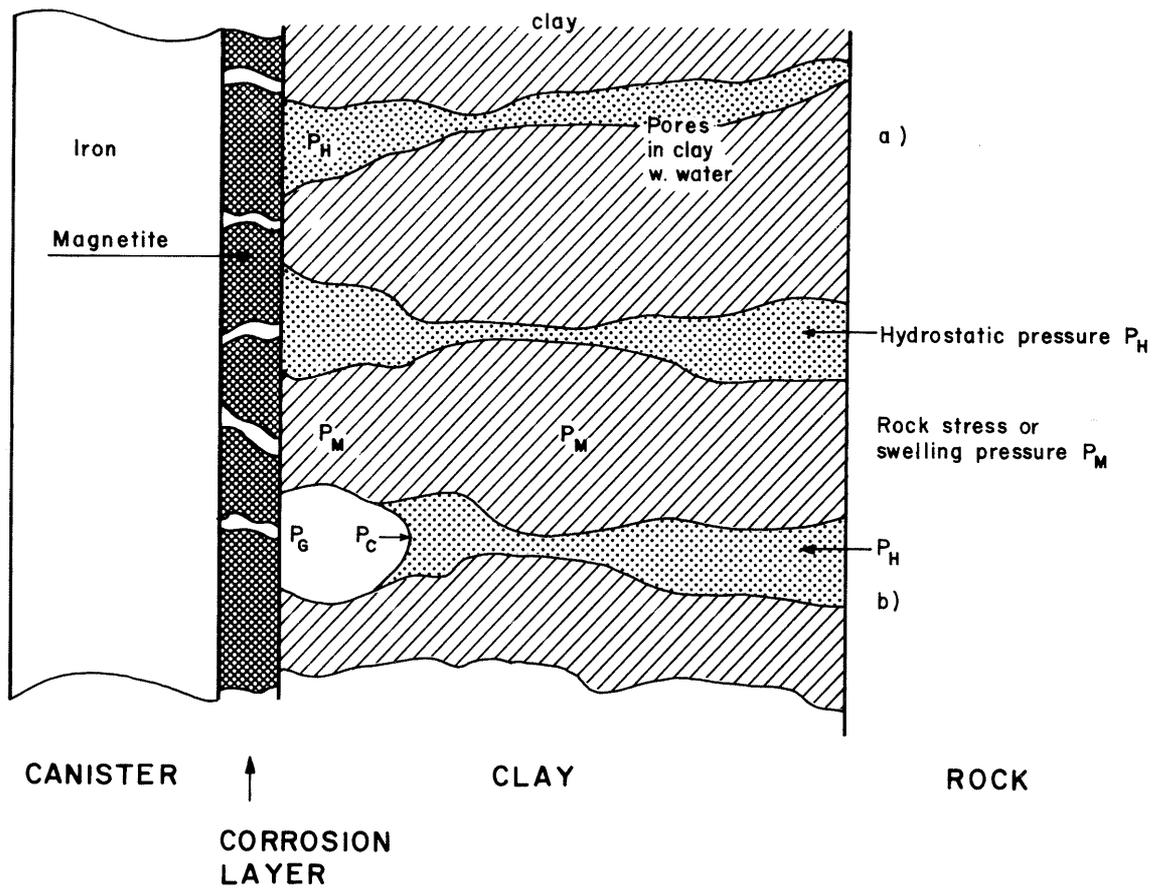


Figure 2: a) Showing the condition when the water in the pores is in direct contact with the canister $P_G < P_H$
 b) Showing the conditions when a gas phase has formed with a pressure P_G . The capillary pressure is P_C .

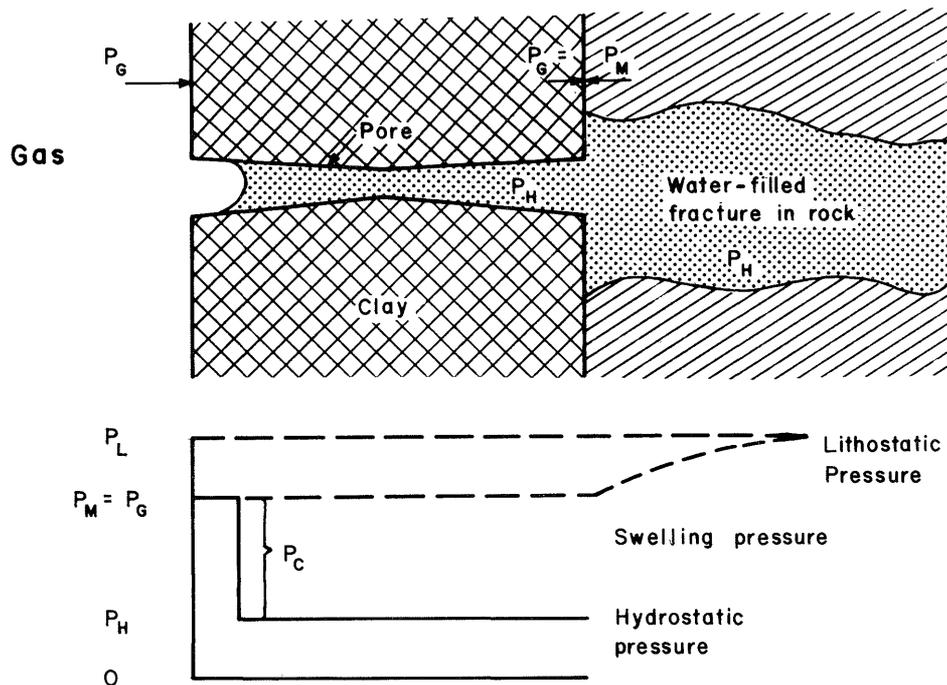


Figure 3: Pressure distribution in the bentonite when the gas pressure P_G exceeds the surrounding hydrostatic pressure P_H but is less than the lithostatic pressure P_L .

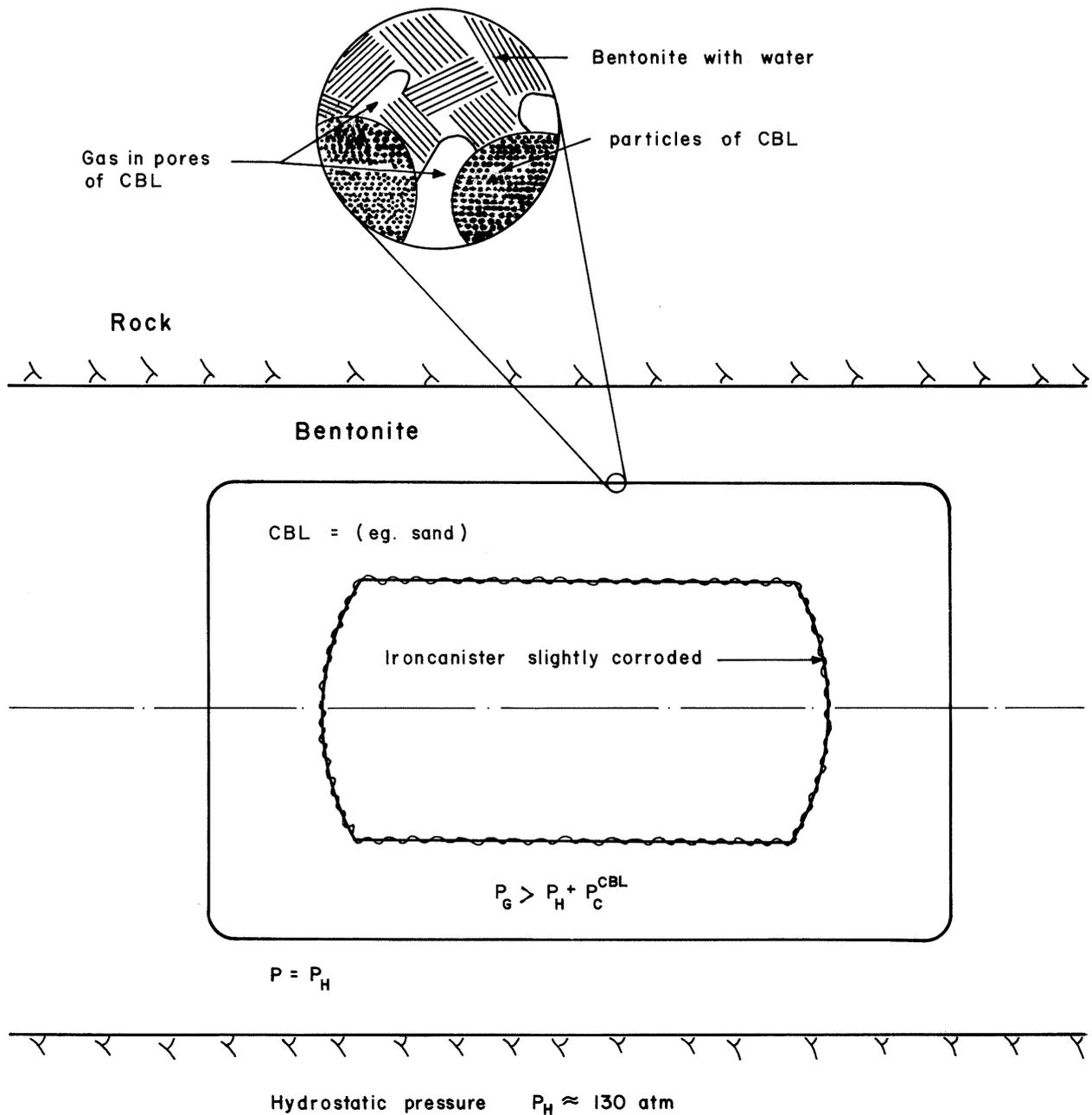


Figure 4: The capillary breaking layer (CBL) has no water in its pores when the gas pressure is higher than the capillary pressure and surrounding hydrostatic pressure.

	K atm	ΔG_r° kcal/mol	ΔH_r° kcal/mol	Reference	
Fe ₃ O ₄ (R1)	} {	630	-15.26*	6.370*	Perry and Chilton 1973
		705	-15.52*	6.600*	Stumm and Morgan 1981
Fe(OH) ₂ (R2)	} {	138	- 2.92	0.734	Perry and Chilton 1973
		50	- 2.32	0.64	Stumm and Morgan 1981
		160	---	---	- " - K-values

$$RT \ln K = \Delta G_r^\circ, \ln (K_{T2} / K_{T1}) = - \Delta H_r^\circ / R / (1/T_1 - 1/T_2)$$

* For 4 molecules of H₂ and H₂O; Divide by 4 for use in equations above.

Table 1: Thermodynamic data for iron-water reactions at 25°C, 1 atm.

	Fe	Fe ₃ O ₄	H ₂ O(l)
M kg/kmol	55.85	231.55	18.02
ρ kg/m ³	7860	5200	997
V m ³ /kmol	$7.11 \cdot 10^{-3}$	$44.5 \cdot 10^{-3}$	$18.1 \cdot 10^{-3}$

Table 2: Densities, molecular weights and molar volumes for iron, magnetite and water at 1 atm and 25°C (Perry and Chilton 1973)

r_0 or δ Angström	P_C atm	a_C
2	7200	$5.4 \cdot 10^{-3}$
4	3600	0.073
6	2400	0.17
10	1440	0.35
20	720	0.59
40	360	0.77
60	240	0.88
100	144	0.91
200	72	0.95

Table 3: The activity of water in circular or slitformed capillaries and the capillary pressure P_C at $T = 298$ K.

Gas constant $R = 1.987 \cdot 10^{-3}$ kcal/mol·K

$R = 82.05$ cm³·atm/mol·K

$R = 8.314 \cdot 10^3$ kg·m²/s²·kmol·K

Kcal to Joule: 4.184 kJ/kcal.

Table 4: Units and unit conversion factors