

# NaCl crystallization at the MgCl<sub>2</sub>/NaCl solution boundary—a possible natural barrier to the transport of radionuclides

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**ABSTRACT.** Concentration, conductivity, temperature, and flow logs from sixteen brine-filled shafts in northern Germany have shown that the brines in all former potash salt mines exhibit a very sharp stratification into lower Mg-rich brine, an upper layer of Na-rich brine, and groundwater at the top. Laboratory experiments have shown that, at the MgCl<sub>2</sub>-brine/NaCl-brine boundary, both solutions become oversaturated with regard to NaCl, due to diffusion processes. NaCl therefore crystallizes from the solutions and forms a salt plug in the boundary region, which considerably reduces further diffusion. It is concluded that the observed effects would also take place in shafts. The backfilling material helps to nucleate the halite crystals and provides a structure on which they might be supported. The results of these experiments show that the density boundaries in the brine bodies act as barriers against transport of matter while the formation of a halite plug growing independently at the MgCl<sub>2</sub>/NaCl-brine interface acts as an additional barrier.

**KEYWORDS:** radionuclides, MgCl<sub>2</sub>, NaCl, brine, halite.

THE air-filled cavities of a final repository mine are not in equilibrium with their surrounding rocks with respect to temperature and lithostatic and hydrostatic pressure. Equilibration of temperature and lithostatic pressure should be reached after backfilling the remaining cavities at the end of the disposal operations.

However, the backfilling material will retain a certain permeability over a longer period, so that there is no hydrostatic pressure balance. Therefore, the possibility still remains that, in a hypothetical case of water inflow, the water may penetrate into the remaining cavities. This water may mobilize particles of the disposed radionuclides and transport them into the biosphere unless mechanisms counteracting their transport become effective. This paper discusses a process which will impede such an occurrence.

*Solution equilibria in water-filled shafts.* A variety

of solution types may be encountered in a given water-filled cavity in salt formations depending on the nature of the adjacent rocks. Intruding water, in contact with potash salt deposits, forms a monovariant four-salt solution at point Q or R of the five-component seawater system. These solutions are referred to as MgCl<sub>2</sub>-solutions in this paper. The Q-solution in the temperature range 25–35 °C, in flooded shafts is saturated with respect to halite, sylvite, carnallite, and kainite. At 25 °C the density of this solution is 1.292 kg/l. The R-solution is saturated with respect to halite, carnallite, kainite, and kieserite, and has a density of 1.311 kg/l at 25 °C (D'Ans, 1933). Calcium sulphates are usually neglected due to their low degree of solubility in MgCl<sub>2</sub>-rich solutions (Eugster *et al.*, 1980).

Above the last outcropping potash salts in the mine, rock salt and calcium sulphates constitute the essential soluble solid phases. The resulting equilibrium solution is therefore saturated with respect to NaCl and CaSO<sub>4</sub>. These solutions are referred to as NaCl-solutions in the following discussion.

Whereas the upper limit of the MgCl<sub>2</sub>-brine in a shaft coincides with the highest potash salt outcrop in the mine the NaCl-solution may exceed the limit of the salt dome and may reach (within the shaft) far into the overburden formations. A layer of groundwater exists above the NaCl-brine, the chemistry of which is less controlled by the salt deposits (Herbert and Sander, 1982). Thin transition layers consisting of mixed solutions may also be found.

The transitions between the individual solutions vary according to local physico-chemical conditions. A shaft may contain several zones of different density and degree of turbulent flow. Solution layers with turbulent flow are distinguished by very uniform temperatures, conductivity, density and chemical composition (figs. 1 and 2). In static layers, however, a distinct conductivity and temperature gradient is observed (fig. 2).

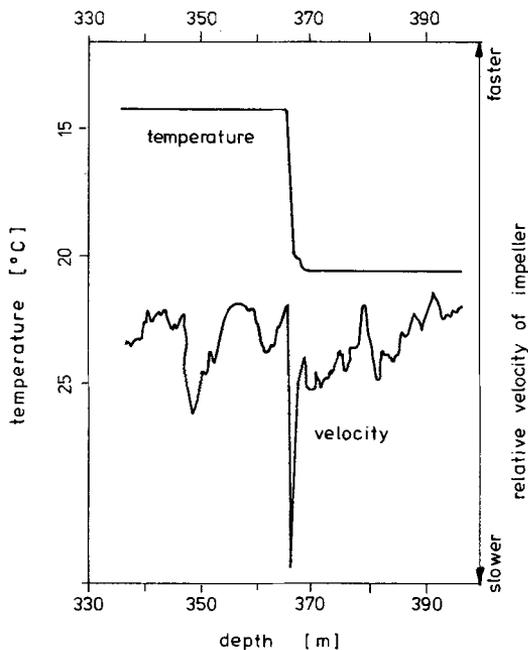


FIG. 1. Temperature and flow plots showing two homogeneous, turbulently intermixed water masses stratified sharply. The temperature above and below the density boundary is uniform in each case.

From laboratory experiments and *in situ* tracer tests it may be deduced that the transport of matter: (a) in static layers takes place by diffusion, i.e. very slowly; (b) in turbulently mixed layers is chiefly a function of flow, i.e. very fast; at the boundaries of the layers the flow reverses; (c) across the boundaries of the layers is essentially due to diffusion, even if each of the two adjacent solutions is in a state of turbulent flow.

A density boundary layer itself constitutes a barrier to the transport of radionuclides.

*Mg<sup>2+</sup> and Na<sup>+</sup> diffusion over the density boundary MgCl<sub>2</sub>/NaCl-solution.* The driving force of diffusion is the varying osmotic pressure due to a concentration gradient. According to Fick's First Law the diffusion flux is proportional to the concentration gradient.

The greatest concentration differences within the water column in a brine-filled shaft are observed in the case of the Mg<sup>2+</sup> ions at the density boundary MgCl<sub>2</sub>/NaCl-solution. Due to the concentration gradient, Mg<sup>2+</sup> will diffuse from the MgCl<sub>2</sub> solution into the NaCl solution. Although both solutions are saturated with NaCl, a diffusion of Na<sup>+</sup> from the NaCl solution into the MgCl<sub>2</sub> solution

also takes place, because the Na<sup>+</sup> concentration in the NaCl solution is considerably higher. The increase of the Mg<sup>2+</sup> content in the NaCl solution causes NaCl oversaturation and consequently precipitation. This is a good illustration of the Gibbs Phase Rule,  $P + F = K + 2$  applied to the system  $MgCl_2 + NaCl + H_2O$  which is unsaturated with respect to MgCl<sub>2</sub>.

The number of the degrees of freedom is 2, namely temperature and the unsaturated component Mg<sup>2+</sup>. Under isothermal conditions the system is a monovariant solution, i.e. the concentration of the saturated components depends on that of the unsaturated components. From this it follows that an increase of the MgCl<sub>2</sub> concentration in the NaCl solution will lead to a NaCl precipitation. The Na<sup>+</sup> concentration difference between the two solutions at the same time leads to a diffusion of Na<sup>+</sup> from the NaCl solution into the MgCl<sub>2</sub> solution. The MgCl<sub>2</sub> solution is an isothermal invariant five-component solution. This also leads to a precipitation of NaCl according to the amount of diffused Na<sup>+</sup>.

The Mg<sup>2+</sup> undersaturation of the MgCl<sub>2</sub> solution as a result of the Mg<sup>2+</sup> diffusion is balanced *in situ* by means of dissolution of Mg minerals such as carnallite and kieserite. The phenomena described above may be considered as a cyclic process which is illustrated in fig. 3. This process, not previously reported, has been investigated in laboratory tests using equipment represented schematically in fig. 4.

For this purpose an NaCl solution was placed above an MgCl<sub>2</sub> solution in a glass vessel. The temperatures of the solutions were adjusted to simulate a shaft section measured *in situ*. Thus, a realistically sharp density stratification was obtained. Diffusion was observed at the density boundary. In order to avoid a cross-sectional reduction, due to crystallization of NaCl which adhered to the wall and the installed temperature sensors in the boundary area, the crystals were constantly removed during the initial stages of the experiment (fig. 5). The Mg<sup>2+</sup> increase with time was measured through an area of 177 cm<sup>2</sup> (fig. 6, curve 1) and the resulting amount of precipitated rock salt calculated (fig. 6, curve 2).

Later the adhering rock salt crystals were no longer removed and that led to the growth of a compact crystal plate at the boundary layer after only 3 weeks. This seal was supported by a rock salt pyramid which had grown on a temperature sensor (fig. 7). The stability of this crystal mass was so high that even after removal of the solutions and dismantling of the equipment it was removed from the tube in an undamaged condition. Furthermore, in the upper part of the model in the NaCl solution

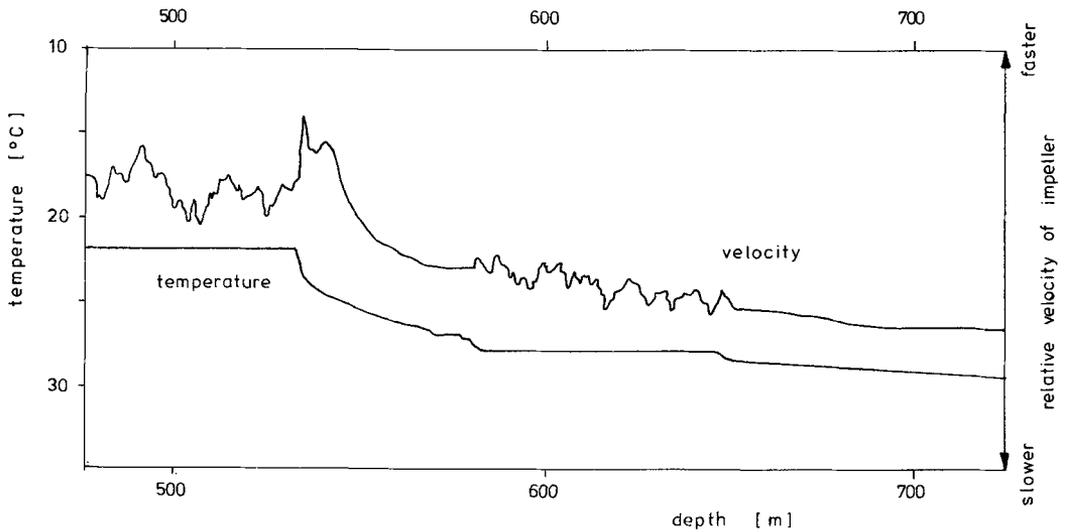


FIG. 2. Temperature and flow plots showing homogeneous, turbulently intermixed water masses alternating with stationary water masses in which a temperature gradient and concentration gradient is observed. Each change of temperature is accompanied by a change of density.

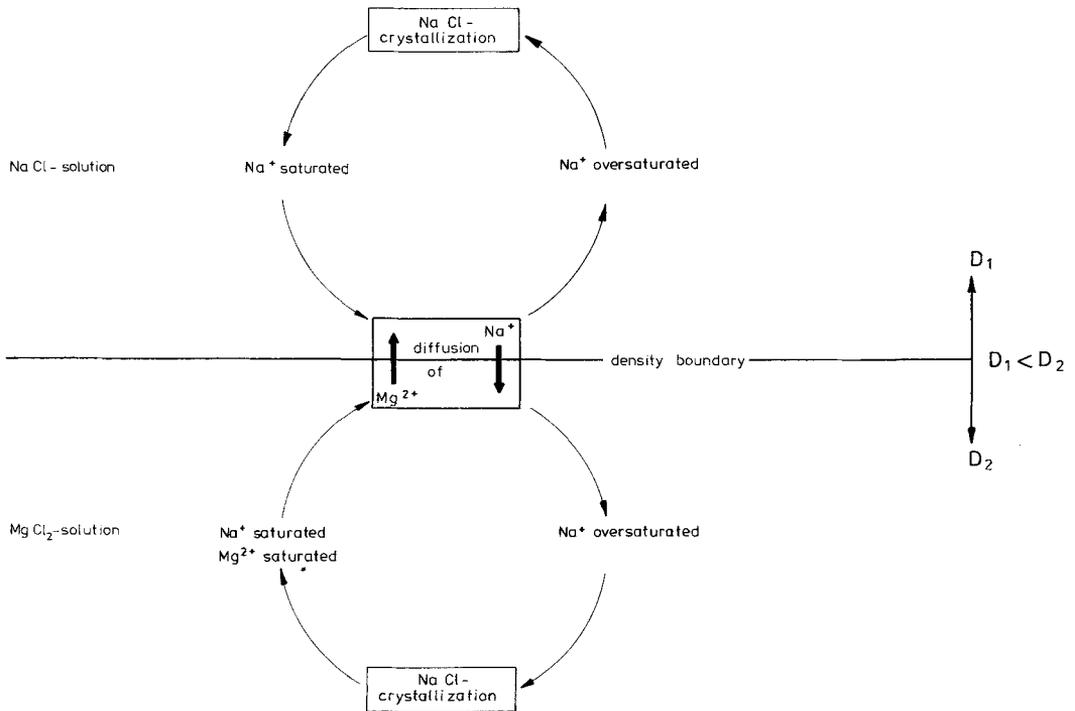


FIG. 3. Schematic representation of the NaCl-forming cyclic process which proceeds by diffusion of  $Mg^{2+}$  and  $Na^+$  through the density boundaries and simultaneous precipitation of NaCl ( $D$  = density).

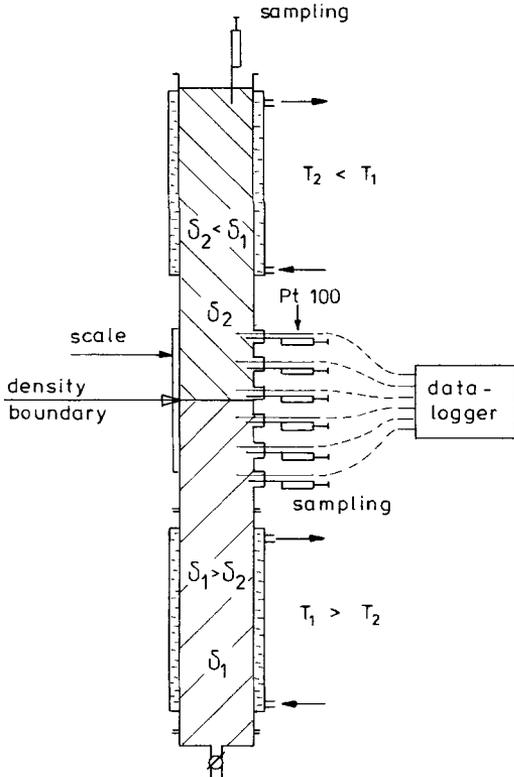


FIG. 4. Schematic representation of the test arrangement for the investigation of diffusion processes at density boundaries. The conditions measured in brine-filled shafts are simulated for: 1. a free water column; 2. a water column backfilled with solid material.

along a sealing ring, which acted as a crystallization-nucleus, a thick, extremely compact ring of crystals developed (fig. 8).

These results are the evidence that the initial theoretical considerations agree with the actual conditions and that the NaCl-generating cyclic process takes place in shafts in which different, NaCl-saturated solutions are encountered.

In the case of a shaft without backfilling material the free cross section is too large to obtain a solid halite plug. Thus, the investigations were also extended to a backfilled glass model containing crushed salt as backfilling material. In this test, which is still in progress, the glass model was filled with rock salt grit of a 4–8 mm sieve-fraction. This backfilling material has a permeability of  $K = 1.2 \times 10^{-2}$  m/s and a porosity of 0.53. Afterwards an NaCl solution was placed above an  $MgCl_2$  solution and the same temperature gradient as in the first test was applied.

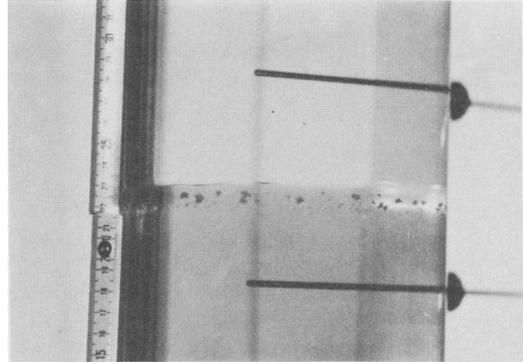


FIG. 5. A stratification simulated in the laboratory in which NaCl solution is placed above  $MgCl_2$  solution. In the vicinity of the very sharp density boundary NaCl crystals have grown on to the wall.

The physico-chemical conditions encountered in the solutions in the model are illustrated by the temperature (fig. 9), density (fig. 10), and specific conductivity curves (fig. 11). It becomes obvious from these curves that, in contrast to the prior test, there were no sharp density boundaries but a nonlinear asymmetric density gradient had formed. The measured  $Mg^{2+}$  increase shows that the diffusion takes place in the same way as in the free glass model, although more slowly (fig. 6, curve 3). Again, from this curve, the crystallized amount of rock salt which is due to  $Mg^{2+}$  diffusion was calculated (fig. 6, curve 4). The portion of secondary halite which is caused by  $Na^+$  diffusion into the  $MgCl_2$  solution cannot be determined by analysis of the  $MgCl_2$  solution, because of the constant  $Na^+$  contents of this NaCl-saturated solution.

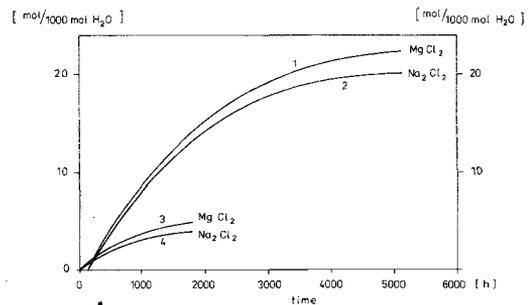
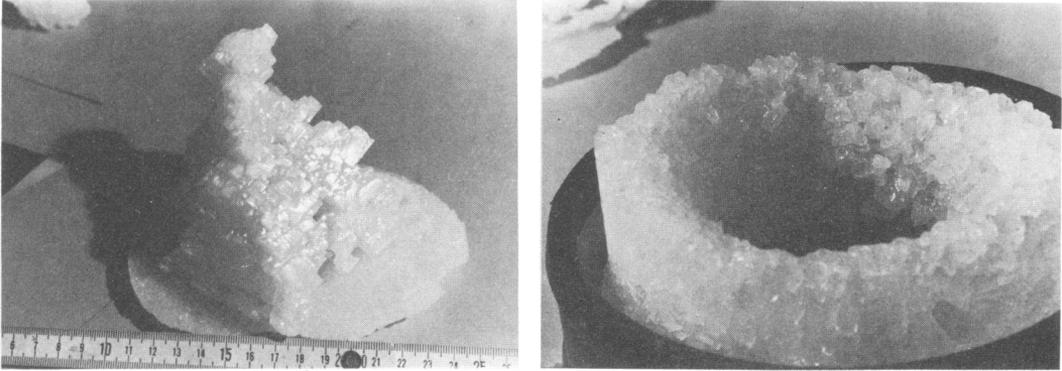


FIG. 6. Curves 1 and 2 were determined in the laboratory in a free water column. Curves 3 and 4 were measured in a backfill under the same conditions. Curves 1 and 3 show an increase in  $MgCl_2$  due to diffusion in the NaCl solution versus time; curves 2 and 4 represent the amount of crystallized NaCl calculated from curves 1 and 3.



FIGS. 7 and 8. FIG. 7 (left). A compact mass of rock salt formed at the density boundary of the NaCl/MgCl<sub>2</sub> solution. It has grown on to a crystal pyramid also consisting of rock salt. FIG. 8 (right). The oversaturation within the NaCl solution, which is due to Mg<sup>2+</sup> diffusion, leads to NaCl-crystallization. A thick ring of halite has formed on a sealing ring acting as a crystallization nucleus.

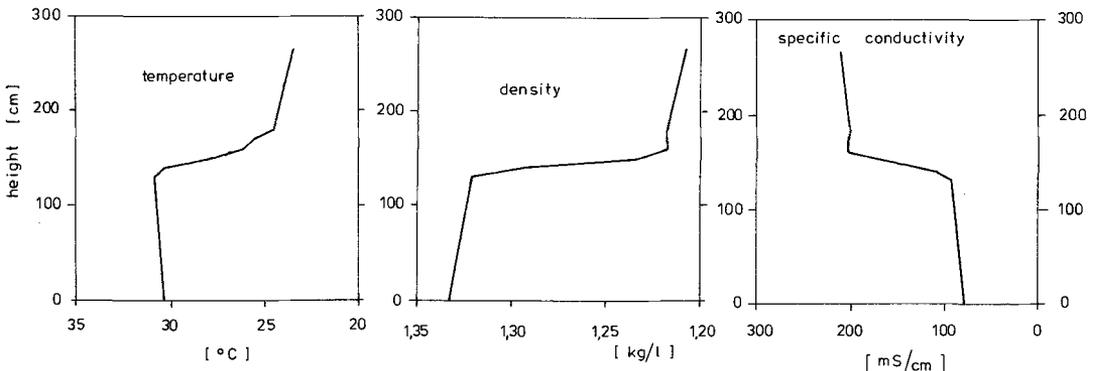
After approximately 50 days it was possible to observe macroscopically, in a zone of about 10 cm height, the first appearance of secondary NaCl crystals in the area of the greatest density changes in the boundary region. After 75 days an obvious densification of the backfilling material took place. Some NaCl crystals even grew at the surface of air bubbles; they initially served as crystallization nuclei and were gradually enclosed by the crystals.

Thus the NaCl-generating cyclic process described above also takes place in the glass model filled with backfilling material and will most probably also lead to formation of a compact seal. These results indicate that this special case of solution

metamorphosis may also occur in a backfilled shaft, as well as in possible solution migration paths in the rocks (as, for example, fissures and permeable anhydrite).

*Evaluation of the natural barrier 'salt plug'.* The salt plug, first discovered and described herein, may act as a dependable barrier to the transport of radionuclides complementing the effect of the density boundaries. In order to assess the NaCl-generating cycle process as a final repository barrier, further tests, especially on a larger scale, must be carried out *in situ*. At present such a barrier would seem to offer the following advantages:

1. It is built up automatically because of the



FIGS. 9-11. FIG. 9 (left). The temperature curve versus the height of the backfilled column displays only a moderate jump of temperature in the transition zone from the MgCl<sub>2</sub> solution to the NaCl solution. FIG. 10 (centre). The density increase with the height of the backfilled column shows an approximately 20 cm thick density gradient. NaCl crystallization can be observed in this region. FIG. 11 (right). The specific conductivity gives an impression of the Mg<sup>2+</sup> distribution in the column, as the specific conductivity decreases despite increasing salt contents with higher Mg<sup>2+</sup> concentration.

geological-mineralogical and physical boundary condition in stratified salt solutions.

2. It possesses the same chemical and thermal properties as the surrounding rock salt.

3. It provides an effective barrier against convective flow.

4. It reduces mass transport during the growth of the plug by continuous diffusion through the decreasing free cross section. As soon as the plug is completely formed, diffusion is effectively stopped at this liquid/liquid boundary, as it is replaced by a liquid/solid system.

5. If the plug is damaged, by tectonic or other mechanical influences, it is self healing. Moreover, the second barrier, i.e. the density boundary, is preserved and therefore effective until the self-healing process sets in.

6. It also forms in natural pathways, independent of the time at which these are formed.

The diffusion of  $Mg^{2+}$  and  $Na^+$  is the most important but not the only process of a solution metamorphosis at this boundary.

The same applies for the other ions present in the solution. Thus gypsum and anhydrite may develop through  $SO_4^{2-}$  and  $Ca^{2+}$  diffusion. In the case of higher concentrations of  $K^+$  and  $Mg^{2+}$ , polyhalite, as well as the Ca-free salts glaserite, leonite, and finally kainite, may also develop.

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