Some Examples of Non-Compatibility of Saline Water and Rock

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ABSTRACT

The enormous amounts of saline mine water obtained as by-product during the exploitation of coal, ore or methane has become a serious and very difficult ecological problem for mining.

There are various methods of solving this problem or diminishing its scale. In spite of rigorous limits imposed by the governments and many technical difficulties, the deep injection of the saline water into the geological strata is the cheapest and therefore the most widely applied method of solving the mine saline water problem.

A very important condition of the success of this method is the compatibility of the injected solution with the rock of the chosen strata. This compatibility requires that there occurs no decrease of the permeability of the rock during the interaction of the introduced solution with the active rock components.

A short discussion of these phenomena and experimental investigation of the interaction of the solution components (various cations) with the active rock components (clay minerals) are the subject of the present paper.

Various concentrations and different cations in the solution may cause the swelling or the shrinkage of the clay mineral part of the sedimentary rock, which may be the source of the permeability change in the flow of these solutions ranging up to two orders of magnitude.

The experimental investigations of these phenomena and their effects, carried out in the Strata Mechanics Research Institute of the Polish Academy of Sciences in Cracow, are reported. The change of the permeability during flow of the various water solutions of salts and natural saline water in the samples of various sandstones and marl carbonate rock are presented in the form of several diagrams.

The conclusions concerning this experimental research are also given.

INTRODUCTION

In many mines all over the world and also in Poland there exists the problem of natural saline water which has to be pumped from mines in order to make possible the exploitation of coal or ore. The concentration of salts in such brine may range from nothing to some dozen percent. The amount of such brine pumped from mines is so great that its disposal into the rivers creates a great deal of damage and danger for the natural environment.

In Poland, e.g. the throw of mine water into the Vistula and Odra rivers amounts to almost one million cubic meter per day. It contains @ 12 400 tons natrium chloride, which with the mean concentration of NaCl @ 1.3 % in the disposal water and at present the relationship between the flow in these rivers and the volume of the disposed of brine gives the mean concentration in the river-water of about 0.3 % NaCl [1]. This has led to a dangerous deterioration of the life in these rivers.

In Poland, the amount of disposed of saline water (near one million cubic meters per day) and very high energy consumption, exclude the possibility of the application of chemical or physico-chemical treatment of these mine waters [1].

Generally, there exists three different ways to prevent or reduce the harmfulness of the pumped brine. The first method leads to reduction of the amount of the pumped mine water by creating some underground screens with reduced permeability in the geological layers surrounding the mine excavations. The second method is to dispose of the water directly into the sea. The third consists in forcing this brine by means of proper wells into some geological water-bearing or brine-bearing layers connected or not-connected with the mine producing the saline water.

The important condition for success of this last method is the absence in the solution of any suspended solid or colloid particles, which due to clogging may lead to an enormous reduction of rock permeability or to general stopping of the flow.

The second important and often underestimated condition is the compatibility of saline water and rocks subjected to the flow of the forced-in solutions.

In the flow of water and water solutions through rocks the permeability may vary with time depending on the kind of the flowing solution. The permeability changes are observed particularly in water flow in sedimentary rocks containing clay minerals, e.g. in sandstones or marl and in water flow in coal containing active components, such as the basic organic matter [2,3,4].

Time-dependent permeability changes in such rocks are always observed after a change in the saturation of the rock with water or after a change in the composition or concentration of the water solution. The magnitude of the observed changes varies and can reach one or two orders of magnitude [2,4].

The change in the properties of the rocks containing clay minerals, due to the change in water content and the change in ion composition in the saturating solution, has been known for a long time [5]. The influence of these phenomena on the permeability in water flow in rocks has been mentioned in literature during the past forty years [6,7,]. There are, however, very few works devoted to the consideration of the permeability changes in water flow in sedimentary rocks [4].

The reason for these permeability changes in water flow in sedimentary rocks are the phenomena of internal swelling or internal shrinkage of the rock, which in turn are the effects of the interaction of water with the active components of the rocks, e.g. with the clay minerals.

A characteristic feature of clay minerals is their high activity to water. This activity is due to their crystalline structure, high degree of dispersity and the shape of the individual grains, which result from their specific crystal structure [5].

When discussing the flow phenomena, the mineral grain should be considered as a complex of a solid body and water bound with it in the form of the surrounding water layer. With this approach the volume changes, that is the swelling of the clay mineral, may imply not only the enlargement of the crystal volume, which may occur e.g. in montmorillonite groups of minerals, but also the enlargement of the volume of the entire complex including the surrounding water layer, which may occur in each of the clay minerals.

In rocks active to water the greatest changes in the permeability in the flow of water or water solutions occur after the originally dry or barely humid rock has been saturated with water. The new, reduced permeability becomes established after a prolonged period of flow, numbering days or even weeks, being the result of water and ions diffusion between the crystal complexes and into the individual mineral particles.

In the flow of water solutions occurring after the rock has been fully saturated, the univalent cations, such as sodium and potassium ions, being exchangeable cations on the surface of clay minerals and between the packets, favor the swelling of these minerals when compared with the bivalent cations.

Calcium and magnesium ions, on the contrary, as exchangeable cations favour the shrinkage of clay minerals by diminishing the amount of water sorbed by them.

The next factor causing the swelling or shrinkage of the clay minerals is the change in the concentration of the solution in contact with the surrounding water layer of these minerals. Increased concentration of this solution (independent of the kind of ions) brings about the shrinkage of the clay mineral-water complex. Conversely, a reduced concentration of the solution causes the swelling of this complex. The greatest internal swelling of the rock occurs after its saturation and in the flow of weakly mineralized, e.g. distilled water.

The effects of the above phenomena: internal swelling of the rock and reduced permeability or internal shrinkage and increase in permeability, following the change in the kind and concentration of ions, have been observed in numerous experiments on the flow of water and water solutions in sedimentary rocks [2,4].

The most typical examples of such permeability changes have been supplied by experimental investigations of the flow of water and some water solutions of salts in sandstones collected from oil reservoirs and rock accompanying coal and ore deposits. The investigations were carried out at the Strata Mechanics Research Institute of the Polish Academy of Sciences in Cracow. The investigations included flows in samples collected from the sandstones of the regions of Southern Poland, from the rocks of the Silesia Coal Basin, as well as from the limestone-clay-dolomite series of Upper Perm layers in Lower Silesia.

EXPERIMENTS

As examples of the implication of the internal swelling and internal shrinkage discussed above, results of experiments carried out with the flow of water and water solutions in samples of some sedimentary rocks are presented.

Experiments were carried out on rock samples in the form of cores with a diameter of 20 to 35 mm. The pressure difference of 0.06 MPa was kept constant during the flows. In the experiments the discharge of flow varying with time after each change in the type of flow, was measured. The actual permeability was calculated from the experimental data (pressure difference, sample dimensions and flow discharge) using Darcy's formula. The results of these experiments are shown graphically, as the change of permeability (expressed in mD, 1 mD = 10^{-15} m^2) with time (expressed in days).

Fig. 1. shows the change of permeability in the flow of water in a previously air-dry sample of sandstone (from an oil-bearing region in Southern Poland), in the flow of 10 % water solution of calcium chloride and at last, again, in the water flow [4].

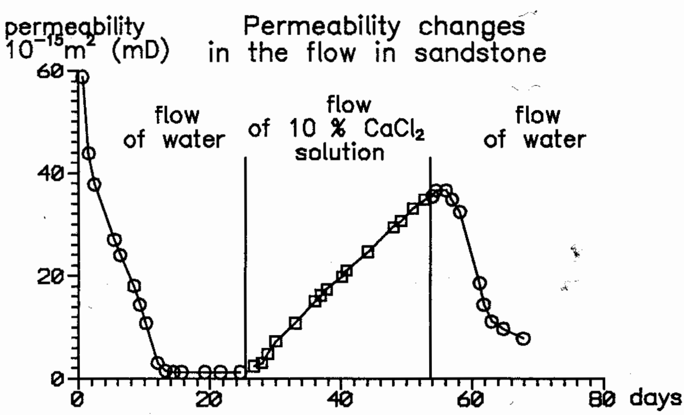

Fig. 1. Permeability changes in the flow of water and calcium chloride solution in a sandstone sample from an oil-bearing region in Southern Poland.

In the water flow the permeability decreased due to the interaction of clay minerals with water and the resulting internal swelling. In the following flow of calcium chloride solution the permeability systematically increased. The bivalent cation and its concentration restrained the swelling and caused the shrinkage of the clay minerals complexes. In repeated water flow the permeability decreased again which was an evidence of the reversibility of the occurring phenomena and their physico-chemical character.

Similar effects can be seen in Fig. 2. which presents the changes in permeability in the flow of calcium chloride solution in a fully saturated and swelled sample of another sandstone (from layers accompanying the coal seams in the Lower Silesia Coal Basin) [4]. The permeability in flow in this experiment increases and the reversibility of these effects is also confirmed in the flow of water.

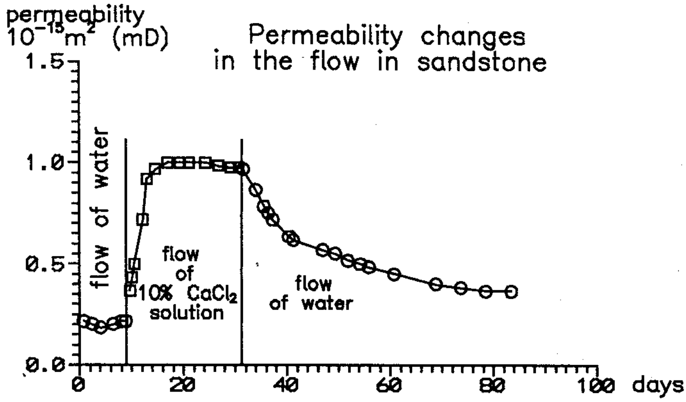

Fig. 2. Permeability changes in the flow of water and calcium chloride solution in a sandstone sample from layers accompanying coal seams in the Lower Silesia Coal Basin.

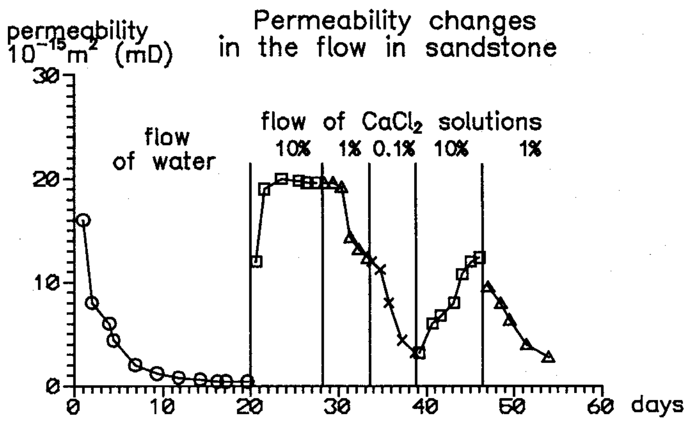

Fig. 3. Permeability changes in the flow of calcium chloride solution of various concentrations in a sample collected from so-called Rotliegendes sandstone.

In Fig. 3. an example of the influence of salt concentration is shown [4]. After the first flow of water and full swelling of the sample (collected from the so-called Rotliegendes sandstone), the following flows of solutions with various concentration of calcium chloride were performed. In the flow of 10 % solution the permeability increased considerably and in the following flows of solutions with lower concentration the permeability decreased systematically and, at last, in a repeated flow of 10 % solution it increased again.

The rules governing the internal swelling and internal shrinkage in the sedimentary rocks are generally valid. Any change in the amount of water in these rocks (humidity or solution concentration) results in a smaller or greater change in the permeability in the flow of the saline water. The phenomena of internal swelling or shrinkage of the rock occur also because of the variation in the ion composition in the flowing solution, e.g. when the relation of the concentration of mono- and bivalent ions is changed. Such variation may be responsible for the non-compatibility of the rock with the flowing solution. When a saline water is forced to flow into the sensitive rock and the composition of ions in this solution is different than that in connate saline water, a smaller or greater internal swelling or shrinkage may occur, changing the permeability in this flow. These changes in permeability depending on conditions may achieve one or two order of magnitude.

Examples of such non-compatibility of solution with rock and the consequences of it are presented.

In the mines of copper ores (Copper Lubin Basin) a great amount of saline water is pumped out (Rudna brine), which has to be disposed of by forcing it into brine-bearing geological layers in limestone-clay-dolomite series of Upper Perm (in Borzecin region, at 1400 m depth). This rock (marl-dolomite, named Borzecin rock) is saturated with connate brine (named Borzecin brine). The salt composition and concentration of the Rudna brine is different from that of the native Borzecin brine.

The Borzecin rock is in ion equilibrium with the flowing Borzecin brine. The permeability in this flow is established. Any change in ion concentration or composition may cause a change in permeability (by internal swelling or shrinkage).

The performed experiments were intended to examine whether the Rudna brine is compatible with the Borzecin rock (being previously in equilibrium with the Borzecin brine). An example of the course of these flows and change in permeability is shown in Fig. 4.

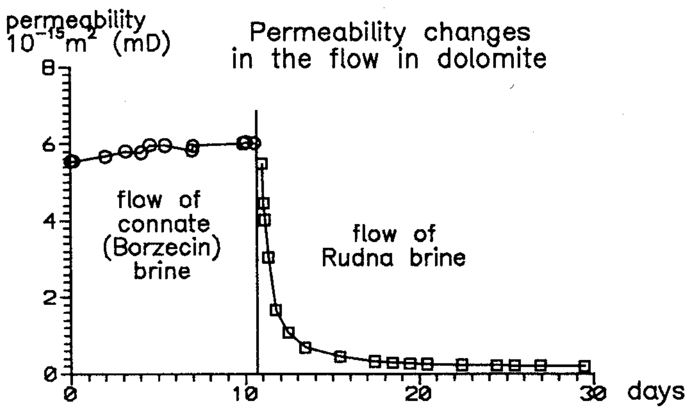

Fig. 4. Permeability changes in the flow of connate (Borzecin) brine and brine (Rudna) pumped from a copper ore mine (Copper Lubin Basin) in sample 1. Collected from marl dolomite series of Upper Perm in Borzecin region.

The first part of this diagram presents the flow of connate Borzecin brine in the Borzecin rock (the sample was air-dry at the beginning of the experiment).

After the permeability in this flow has been established, the flow of Borzecin brine is exchanged by the Rudna brine flow, (modelling the forcing-in of this brine). From this moment the permeability begins to change.

The next part of the diagram shows this permeability change in the flow of the Rudna brine forced into the Borzecin rock. On the first day of flow the permeability decreases almost five times. In the course of further flow permeability decreases more slowly, but after ten days it diminishes more than twenty times.

The experiment gives a definite result: the Rudna brine is not compatible with the Borzecin rock. Forcing-in this brine into this rock results in a significant decrease of permeability.

What is the reason for this non-compatibility ? The Borzecin rock is a marl-dolomite with a not too great content of clay minerals (difficult to be measured), but sensitive. The connate Borzecin brine comprises 16.5 % of natrium chloride and 4.1 % of calcium and magnesium chlorides together. The concentration of natrium chloride in the forced-in Rudna brine is a little smaller, namely 12 %, but the concentration of calcium and magnesium chloride together is considerably lower being equal to 1.2 %.

In general, salt concentration in Borzecin brine (21 %) is greater than that in the Rudna brine (13 %). Moreover, the relation of an equivalent concentration of natrium cation to the calcium-magnesium cations in the Borzecin brine ($Na^+/Ca^{2+}+Mg^{2+}$ = 11) is considerably smaller than such a relation in the Rudna brine ($Na^+/Ca^{2+}+Mg^{2+}$ = 24). This is undoubtedly the source of a considerable exchange of the bivalent cations Ca^{2+} and Mg^{2+} into the monovalent natrium cations in the Borzecin rock during the flow of the Rudna brine.

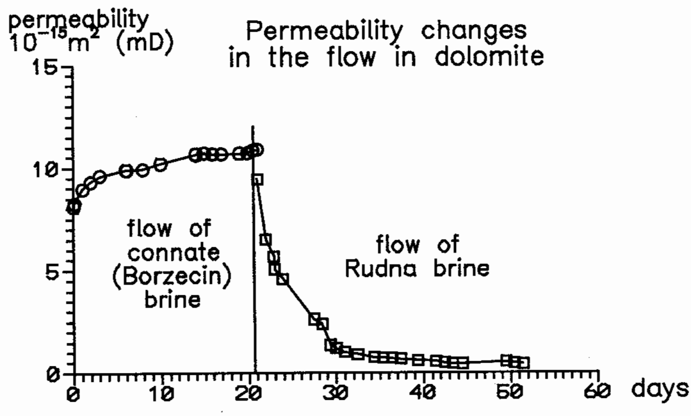

Fig. 5. Permeability changes in the flow of connate (Borzecin) brine and brine (Rudna) pumped from a copper ore mine (Copper Lubin Basin) in sample 2.
Collected from marl-dolomite series of Upper Perm in Borzecin region.

Both existing differences: in the general salt concentration and in the cation composition, favor the internal swelling in the rock, being the origin of permeability decrease.

The next example of a similar picture of the permeability decrease in the flow of Rudna brine in another sample of the Borzecin rock is presented in Fig. 5. The course of the change in permeability as the result of the performed flow is the same as in the previous sample.

The result of the flow of the Rudna brine in the Borzecin rock sample (air-dry at the beginning) without the previous saturation with connate Borzecin brine, is shown in Fig. 6. There occurs also a considerable permeability decrease caused by sorption of water and cation exchange establishing new equilibrium between the rock and the flowing brine.

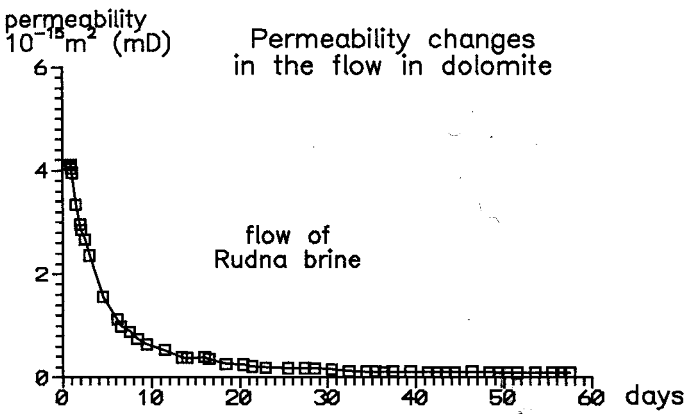

Fig. 6. Permeability changes in the flow of brine (Rudna) pumped from a copper ore mine (Copper Lubin Basin) in sample 3.
Collected from marl dolomite series of Upper Perm in Borzecin region.

CONCLUSIONS

Time-dependent permeability changes in sedimentary rocks during the flow of water and various salt solutions are observed in many experiments. Considerable changes occur when the kind and/or the concentration of cations in the flowing saline water have been changed. The origin of these changes is the cation exchange in the active part of the rock which is the source of changes in the amount of the sorbed water determining the internal swelling or shrinkage of the rock. This in turn is the cause of the decrease or increase of the permeability in the flow of this saline water.

Thus, the forcing-in of some brine into the sedimentary rock, being previously in equilibrium with different saline water, may result in the change of permeability in this flow ranging up to as much as two orders of magnitude (Figs 4. to 6.).

This compatibility or non-compatibility of forced-in saline water with the rock may decide about the success of the process of water disposal in the rocks.

In the case when fracture permeability is significant, the effect of non-compatibility may be insignificant. In any case however, the internal swelling of the rock caused by the non-compatibility of the solution with the rock may diminish the total capacity of the rock to receive the solution.

These phenomena ought to be taken into account when planning and utilizing such disposal processes.

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