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## IONIC ADSORPTION OF SAND- AND CLAYSTONES

### Introduction

It is well-known that the contamination of soils or rocks, developing as a result of industrial, agricultural or some other activity, is a significant environmental problem. The task in these cases is to determine the kind and the amount of the contaminating element as well as to indicate its areal distribution. To complete these tasks, it is necessary know how the different soils and rocks do adsorb different ions, with a special regard to the toxic elements. We mention here only a few examples from the large amount of papers on this topic [1], [2], [3]. Our own experimental results [7], [8], [9] as well as the requirements for environmental mapping [6] have proven the necessity and importance of these experiments. The importance of ionic adsorption is demonstrated by the fact that research on this topic have a high priority in the US [4], [5].

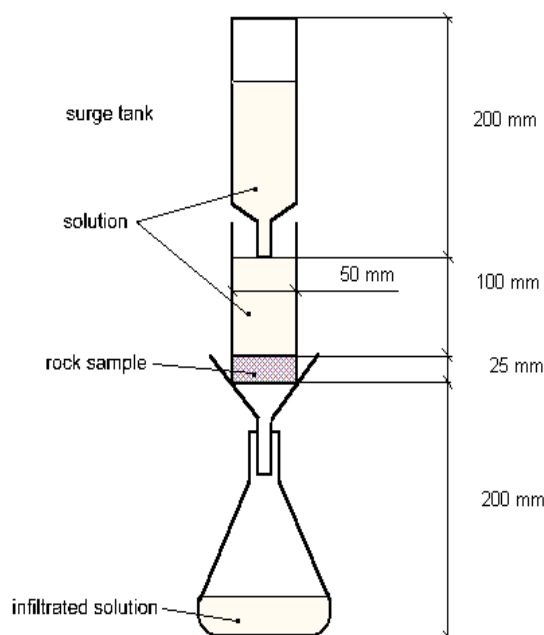
Experimental results on ionic adsorption of certain rocks are presented in this paper. Several cations were investigated in different anionic environments. It has to be mentioned that precipitation of minerals in a small amount takes also place parallel with the adsorption. However, since it was not possible to distinguish these processes, we consider later the phenomena as adsorption, whether precipitation occurs or not.

### THE EXPERIMENTAL METHOD

As schematically shown in **Fig. 1**, solutions with different cation contents were percolated through the rock sample from a liquid tank of constant level. The constant level of the solution (100 mm) was secured by the upper surge tank.

The ionic content of the infiltrated solution percolated through the sample was measured continuously. Comparing the concentration of the infiltrated solution with that of the initial one, the ionic adsorption of the rock sample can be measured. The cation content of these solutions were determined by atomic absorption method.

The quantity of the rock samples examined was 100 grams for sand and perlite and 50 grams for other rocks. The initial cation concentration of the solution



**Fig. 1.** Sketch of the experimental equipment

for all investigated elements, such as  $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$  was 30 mg/l for sand and perlite samples while 70 mg/l for other rocks. Concentration of the two examined anions: sulfate and chloride was determined by the stoichiometry of the solution.

Table 1. summarises the main petrophysical features of the rock samples examined, such as the rock type and locality, the abbreviated code, the characteristic grain size (median;  $D_m$ ), the average specific gravity of the particles ( $\rho$ ), the specific surface of the grains for  $G=100$  g mass calculated by the  $F = \frac{6G}{D_m \rho}$  formula. The mineral composition

of the samples determined by XRD ( $Co_{K\alpha}$ ) and thermoanalysis (DTA) methods is shown in Table 2., while Table 3. summarises the chemical composition of the samples.

**Table 1**

**Petrophysical characteristics of the examined rocks**

| <i>Rock type and locality</i>                                    | <i>Abbreviated code used</i> | $D_m$ ( $\mu m$ ) | $\rho$ (Mg/c.m) | $F$ (sq.m/100g) |
|--|------------------------------|-------------------|-----------------|-----------------|
| Clayey lignite, Bükkábrány                                       | <i>B1</i>                    | 125               | 1.90            | 2.52            |
| Grey clay, Bükkábrány  | <i>B2</i>                    | 5                 | 2.25            | 47.06           |
| Brown clay, Bükkábrány   | <i>B3</i>                    | 12                | 2.50            | 20.00           |
| Brick clay, Mályi  | <i>T4</i>                    | 4                 | 2.50            | 60.00           |
| Brown clay, Helyőcsaba<br>Cement Works Co.                       | <i>C5</i>                    | 60                | 2.45            | 4.08            |
| Red clay, Mátramindszent   | <i>D6</i>                    | 8                 | 2.50            | 30.00           |
| Altered rhyolitic (clay- and<br>zeolite-bearing) tuff, Székvölgy | <i>Z7</i>                    | 250               | 2.40            | 0.98            |
| Pure (washed out) sand   | <i>H8</i>                    | 400               | 2.62            | 0.54            |
| Clayey sand  | <i>M9</i>                    | 180               | 2.60            | 1.28            |
| Perlite  | <i>P10</i>                   | 500               | 2.00            | 0.60            |

**Table 2**

**Mineral composition of the samples (weight %)**

| <i>Minerals</i> | <i>B1</i> | <i>B2</i> | <i>B3</i> | <i>T4</i> | <i>C5</i> | <i>D6</i> | <i>Z7</i> | <i>H8</i> | <i>M9</i> | <i>P10</i> |
|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|------------|
| Montmorillonite | 20        | 5         | 10        | -         | -         | -         | 5         | -         | 5         | -          |
| Illite          | 10        | 25        | 10        | 25        | 20        | 20        | -         | -         | 5         | -          |
| Chlorite        | 10        | 20        | 10        | 20        | -         | -         | -         | -         | 5         | -          |
| Kaolinite       | -         | -         | -         | -         | -         | 25        | -         | -         | -         | -          |
| Quartz          | 10        | 45        | 50        | 45        | 40        | 45        | -         | 85        | 60        | -          |
| Feldspar        | -         | 5         | 5         | 5         | 5         | 5         | -         | 10        | 5         | -          |
| Calcite         | -         | -         | 10        | -         | -         | -         | -         | -         | -         | -          |
| Cristobalite    | -         | -         | -         | -         | -         | -         | 40        | -         | -         | -          |
| Vermiculite     | -         | -         | -         | -         | -         | -         | 15        | -         | -         | -          |
| X-ray amorphous | 50        | -         | 5         | 5         | 10        | 5         | 50        | 5         | 10        | 100        |

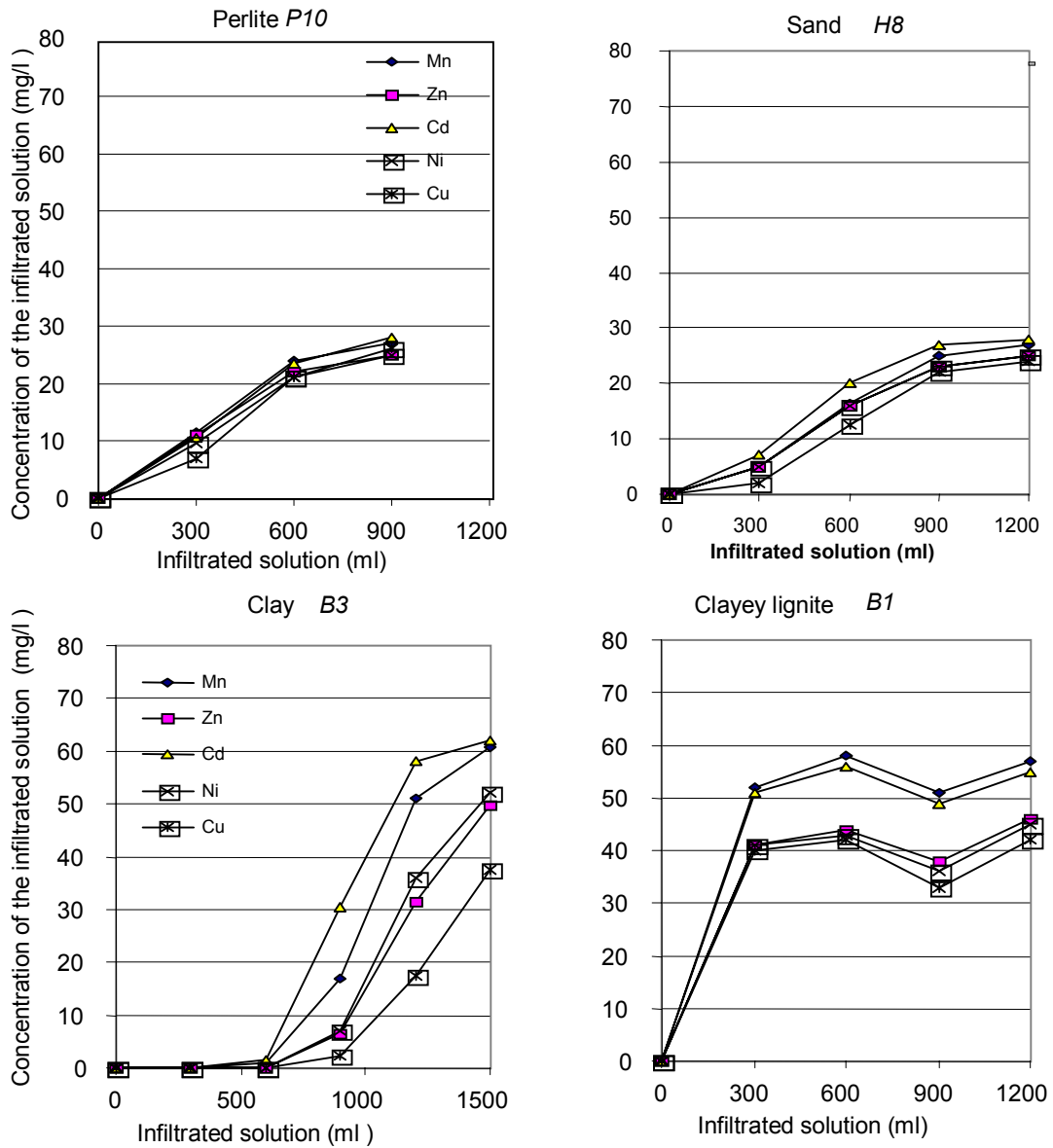
**Table 3****Chemical composition of the samples (weight %)**

|                                | <i>B1</i> | <i>B2</i> | <i>B3</i> | <i>T4</i> | <i>C5</i> | <i>D6</i> | <i>Z7</i> | <i>H8</i> | <i>M9</i> | <i>P10</i> |
|--------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|------------|
| SiO <sub>2</sub>               | 27,46     | 57,04     | 65,76     | 59,42     | 67,08     | 54,60     | 67,25     | 91,81     | 72,28     | 74,32      |
| Al <sub>2</sub> O <sub>3</sub> | 7,22      | 20,52     | 14,45     | 17,10     | 14,92     | 20,89     | 15,96     | 4,27      | 13,02     | 13,50      |
| Fe <sub>2</sub> O <sub>3</sub> | 5,86      | 4,26      | 4,69      | 5,58      | 4,39      | 7,49      | 3,52      | 0,70      | 4,15      | 1,20       |
| MnO                            | 0,05      | 0,05      | 0,12      | 0,10      | 0,04      | 0,08      | 0,03      | 0,00      | 0,05      | 0,01       |
| MgO                            | 0,73      | 0,72      | 0,98      | 2,15      | 1,45      | 1,89      | 0,85      | 0,01      | 0,26      | 0,01       |
| CaO                            | 2,02      | 0,73      | 1,61      | 1,92      | 0,85      | 1,43      | 0,77      | 0,54      | 1,22      | 1,15       |
| Na <sub>2</sub> O              | 0,14      | 0,62      | 0,82      | 0,64      | 1,02      | 0,24      | 0,85      | 0,73      | 1,47      | 1,15       |
| K <sub>2</sub> O               | 0,51      | 2,88      | 1,68      | 2,64      | 2,04      | 3,28      | 1,18      | 1,05      | 2,01      | 3,30       |
| ignition losses                | 55,67     | 11,65     | 9,31      | 9,83      | 7,73      | 9,41      | 10,51     | 5,98      | 4,98      | 3,30       |
| Total                          | 99,61     | 99,47     | 99,42     | 99,38     | 99,52     | 99,31     | 99,49     | 99,92     | 99,44     | 99,73      |

**RESULTS**

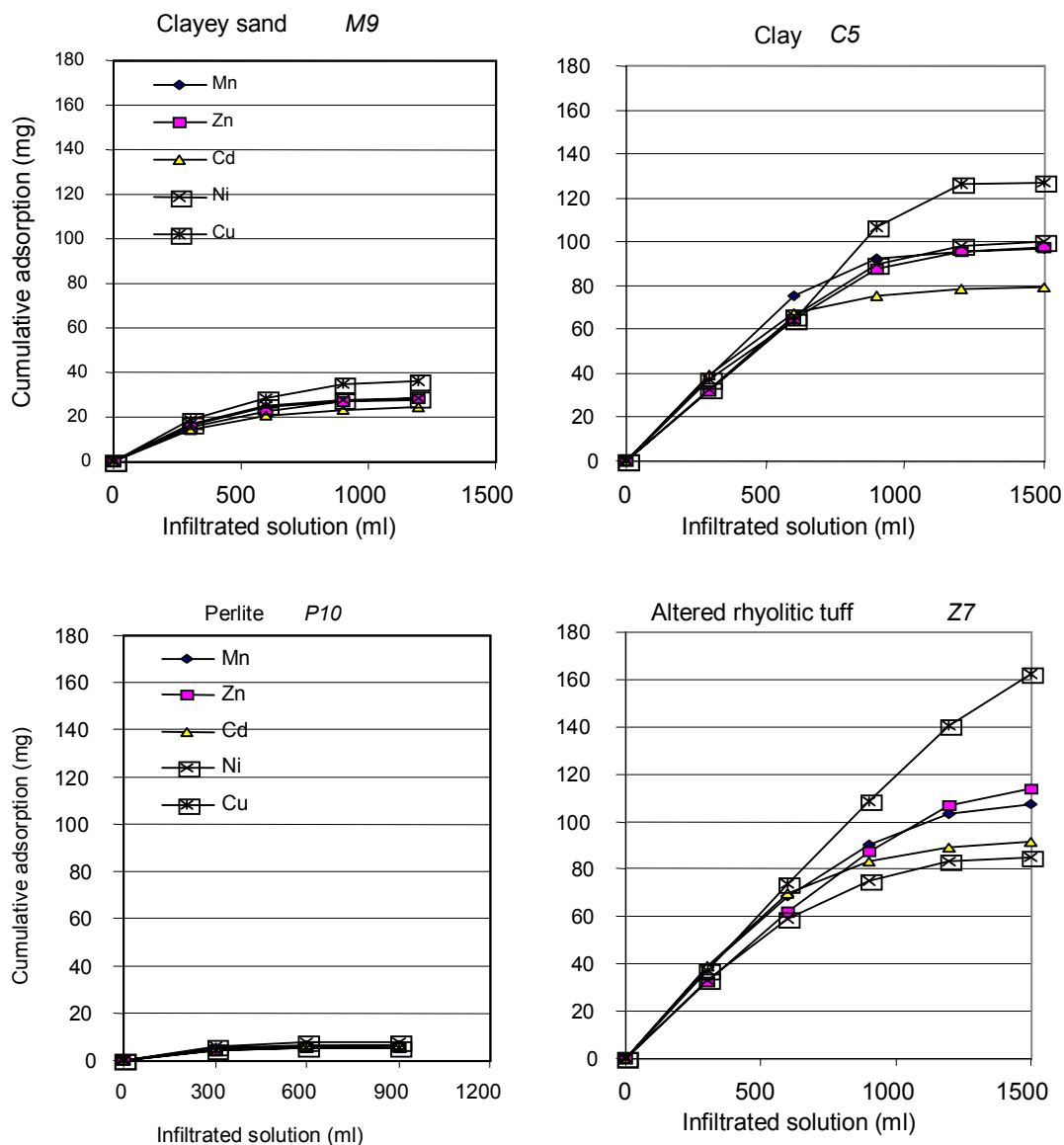
Charts on **Fig. 2.** show for a few investigated rock types that after the percolation of a certain amount of solution, the concentration of the infiltrated solution approaches the concentration of the initial one. It is clear from the figure that the concentration of the solution infiltrated through the clay *B3* is practically zero after the percolation of 600 ml solution, whilst that reaches 60-80% after 1200 ml. On the other hand, clay *B3* at the initial phase adsorbs the whole percolating ion content, whilst the clayey lignite *B1* adsorbs much less. (More intensive adsorption was expected for the latter sample due to its high carbon content.)

Experimental results on the perlite *P10* and the pure (washed out) sand *H8* show that after percolation of 300 ml solution, the concentration of the infiltrated solution compared to the initial one is one third and 10%, respectively. Concerning the examined cations, they are adsorbed at the same rate in these two rock types, since the change in ionic concentration of the infiltrated solutions as a function of the amount of infiltrated solution is practically identical. Conversely, the manganese and cadmium cations compared to the others are adsorbed in a lesser amount in the clayey lignite *B1* (see **Fig. 2.**).



**Fig. 2.** Concentration changes of the infiltrated solution as a function of the amount of infiltrated solution for different rocks. Anion: chloride.

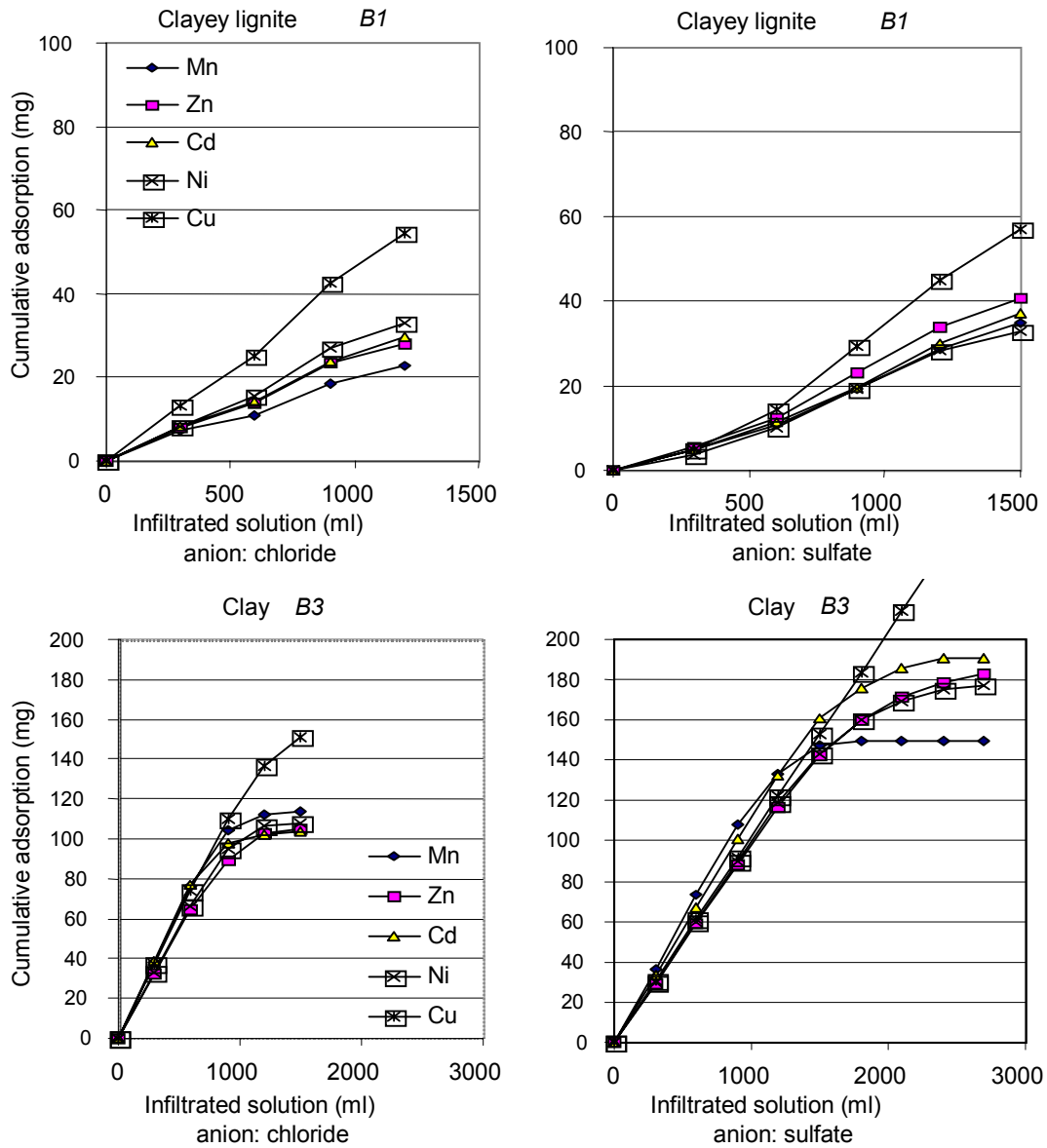
The cumulative adsorption curves calculated from the experimental results for different rocks are shown in **Figs. 3, 4 and 5.**



**Fig. 3.** Cumulative adsorption of cations calculated for 100 g rock mass as a function of the amount of infiltrated solution. Anion: chloride.

Fig. 3 demonstrates the cumulative adsorption i.e. the total amount of adsorbed cations in a 100 g rock sample as a function of the amount of the infiltrated solution, for the clayey sand *M9*, clay *C5*, perlite *P10* and altered rhyolitic tuff *Z7* samples. It is clear from the figure that adsorption of the clayey sand *M9* and perlite *P10* is small, whilst that is high for the clay *C5* and for the altered rhyolitic tuff *Z7*. Adsorbing capacity of the last one is the highest as it has been expected. A common feature of the rocks included in **Fig. 3.** is that adsorption of copper ions is the most intensive process. In the clay sample *C5* this is followed by the adsorption of nickel, manganese and zinc ions at the same rate and by the adsorption of cadmium at the lowest rate. Conversely, the altered rhyolitic tuff sample *Z7* adsorbs the cations in the zinc - manganese - cadmium - nickel order, while all curves differ from another. Adsorption of different cations by the perlite *P10* and clayey sand *M9* samples is small and quite similar. These charts show that after a certain amount of infiltrated solution, the cumulative adsorption value

remains constant, thus the rock practically becomes saturated and does not or barely incorporates further cations.

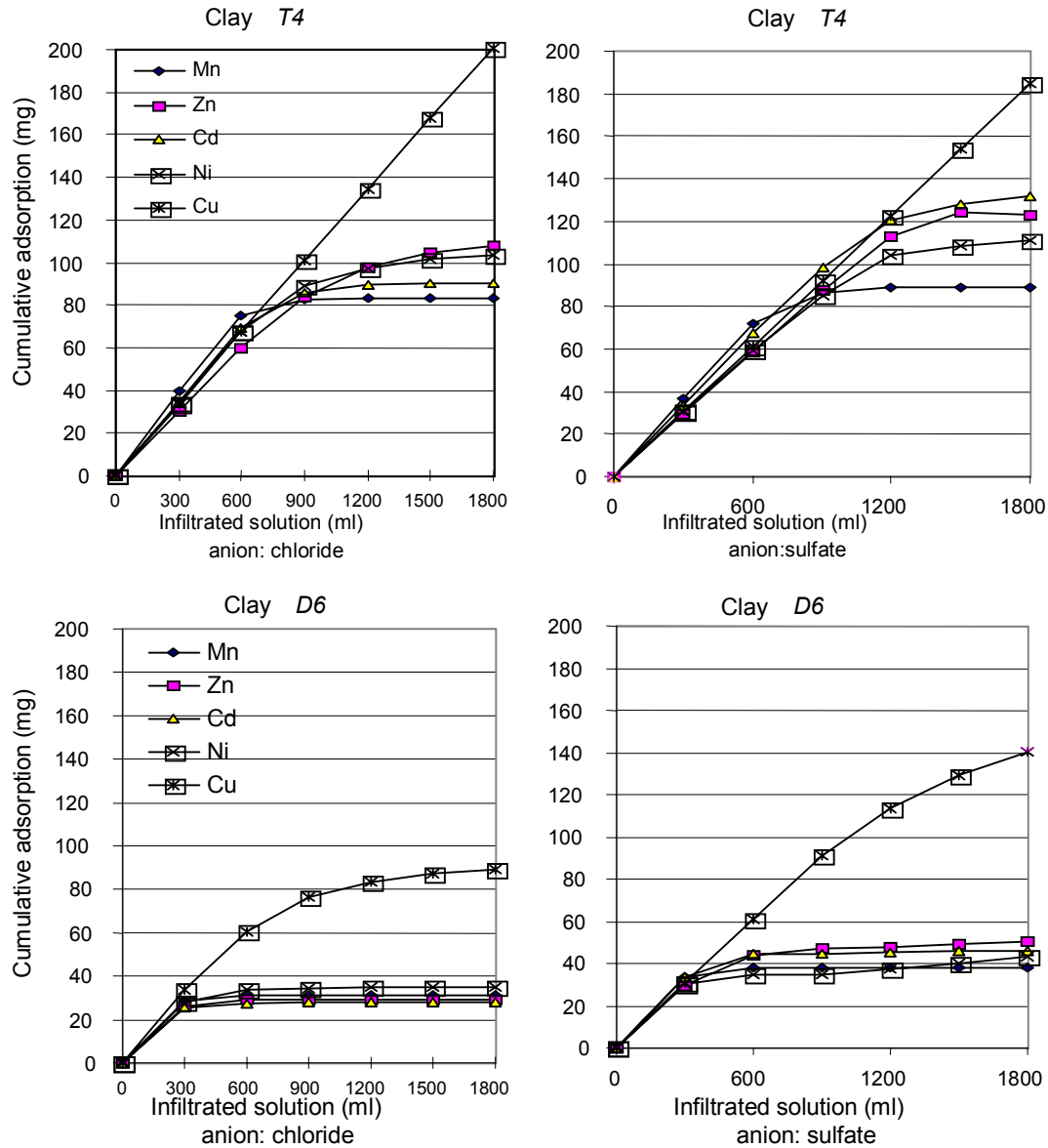


**Fig. 4.** Cumulative adsorption curves of cations for two rock samples in chloride (left) and sulfate (right) environment.

Experiments shown in **Figs. 2.** and **3.** has been completed in chloride environment. Considering the supposition that adsorption depends also on the kind of anion, experiments were completed with another common anion: sulfate as well. Cumulative adsorption curves that illustrate the behaviour of certain rock samples both in chloride and sulfate environments are shown in **Figs. 4** and **5**. It is clear from these figures that the clay sample *D6* becomes saturated for manganese, zinc, cadmium and nickel after percolating about 600 ml solution, and adsorption does not occur during further

percolation. The clay sample *B3* behaves similarly after percolating 1000-2000 ml solution, while in the clay sample *T4* this phenomena takes place over 1000-1400 ml.

Adsorption behaviour of the clayey lignite *B1* is quite similar for chloride and sulfate environments (upper part of **Fig. 4**). Adsorbing capacity of the clay sample *B3* is much higher in sulfate environment (lower part of **Fig. 4**). Experimental results on clay *T4* show that copper is adsorbed less intensively in sulfate environment, however all other examined cations have a greater adsorption in sulfate environment than in chloride one (upper part of **Fig. 5**). The case of the clay sample *D6* is similar, however



**Fig. 5.** Cumulative adsorption curves of cations for two rock samples in chloride (left) and sulfate (right) environment.

in this case the adsorbing capacity of all cations - copper as well - is higher in sulfate environment (lower part of **Fig. 5**).

The experimental results show that adsorption increases parallel with the increasing of specific surface, thus larger specific surface results in higher adsorbing capacity.

## CONCLUSION

Based on the experiments, the followings can be stated:

The adsorbing capacity depends on the rock properties since sand, perlite and even clayey lignite had a much lower adsorption than any clay sample. Exception from this trend is the kaolinite-bearing clay, because adsorption of that is similar to the adsorption of the clayey sand or the clayey lignite.

A general trend is that the adsorption is high at the initial phase. The more solution is percolated, the less cations are adsorbed in the sample. The adsorption can even be terminated after the percolation of a certain amount of solution.

The most intensively adsorbed cation is copper, the adsorbing capacity of the other examined cations are less and match each other.

Adsorbing capacity depends significantly on the kind of the anion in the solution.

Summarising: the most important result of the experiments is that the incorporation of cations terminates after the percolation of a certain amount of solution (which overrides 20-40 times the rock mass). The cumulative adsorption could significantly be increased by increasing the rock mass, which condition is given at the nature. Based on experimental data and supposing 2 Mg/c.m specific gravity, a 1 c.m rock body can adsorb 20,000 times more cations than that took place at the experiments. Consequently loosened, common clay masses are able to adsorb 1-2 kg cations per c.m. Supposing a barely probable case that adsorbing capacity of naturally occurring clays is only one fifth of the loosened ones investigated in the experiments, they also can adsorb at least 0.5-1 kg cations per c.m. It means that a clay body of some hundred cubic metres is capable to adsorb a significant contamination, thus the contamination can be diffused only within a relatively small area.

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