

# On Cation Exchange Capacity Determinations using the Radiotracer Method with Calcium-45

by

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## Abstract

In many investigations of clay sediments, the determination of the cation exchange capacity of the clay fraction is of great value. Some years ago Dr. I. TH. ROSENQVIST developed a method in which the cation exchange capacity is determined by means of a radiotracer technique using Ca-45 as tracer. This method is now used in investigations of Danish clays. The clay fraction of Danish clays often contains calcite and sometimes gypsum, and since the clay fraction in addition may contain various other non-clay minerals, the "cation exchange capacity" of a series of non-clay minerals is determined. The results are given in Tables 1 and 2.

In mineralogical and technical investigations of clay sediments and clay minerals, the determination of the cation exchange capacity is often of great value. In 1949 Dr. I. TH. ROSENQVIST, head of the Research Laboratory of the Norwegian Geotechnical Institute, Oslo, developed a quick and reliable quantitative method according to which the determination is carried out by using a radiotracer technique with calcium-45 as tracer. This technique is now used in the laboratories of the Mineralogical-Geological Institute (University of Copenhagen), where it has been of great help and has given good results.

However, certain difficulties arose in the determination of the cation exchange capacity of different clays, as repeated determinations of the same clay sample gave rather scattered results. As an example of this, determinations of a Danish tertiary clay gave results varying within 60-90 meqv/100 gr.

Since the sample contained some gypsum crystals, it was presumed that the variation was dependent upon these.

Numerous Danish clays contain calcite, and many clays contain gypsum (BØGGILD 1943). Both these and other non-clay minerals have been observed in the clay fraction of Danish clays (CLAUSEN 1932, UNMACK 1944, 1947 and 1949, GRAFF-PETERSEN 1955). On the electronmicrograph

(Fig. 1), gypsum crystals (or cleavage flakes) with the longest edge of  $0.5\mu$  are seen from a Danish clay. In addition, MACEWAN (1951) gives a list of non-clay minerals likely to occur in the clay fraction.

To determine the influence of some of these minerals on the cation exchange capacity (at pH 6.5), pure mineral samples were pulverized ( $> 5\mu$ ), and each mineral powder was treated in the same way as the clay samples in the adsorption determinations.

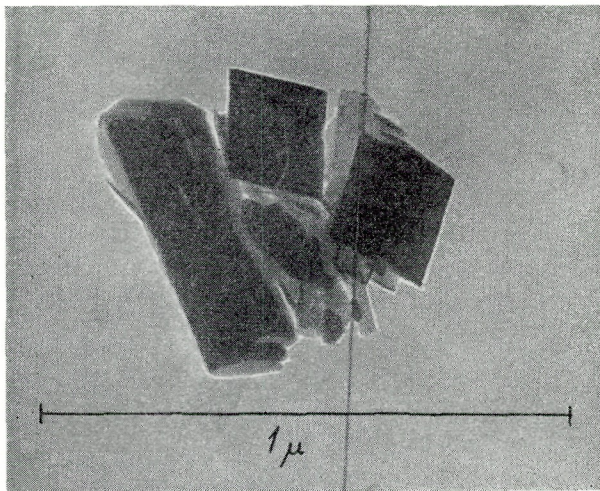


Figure 1. Electronmicrograph (70000 X) showing gypsum crystals (or cleavage flakes) with the longest edge of  $0.5\mu$ .

The procedure is clearly described by ROSENQVIST (1954 and 1955), and since essentially the same method is used in the investigations here treated, reference is made to ROSENQVIST's papers.

For the determinations a series of standards on 2.5-5-10-20-50-75 and 100 meqv/100 gr was prepared, since the relation between the measured activity and the Ca-45 concentration is not constant at a rising concentration, depending on the resolving time of the G.M.-counter.

The radiocalcium solution (6 meqv in 6 ml) was added to the mineral powders (0.5 gr) and vigorously shaken. The samples remained in the solution until all were mixed. Then they were centrifuged and rinsed. In this way every mineral powder was treated in the radiocalcium solution for approximately 25 minutes. The results of 10 investigated minerals are given in Table 1.

It is seen that the calcium free minerals have adsorbed less than 1 meqv/100 gr. The calcium bearing minerals have "adsorbed" varying amounts, from 2.1 to 104.2 meqv/100 gr. The minerals anortite, apatite and dolomite, which are scarcely active in the presence of water, have taken up a relatively small amount of radiocalcium, whereas calcite and gypsum have taken up a considerable amount.

Gypsum is somewhat soluble in water, and calcite is partly soluble

in CO<sub>2</sub>-containing water. When the radioactive solution is made (dissolving CaCO<sub>3</sub> in hydrochloric acid), some CO<sub>2</sub> will be dissolved in the liquid with the result that it will be more aggressive to calcite than pure water is.

As the solubility thus seems to have an influence on the exchange of inactive calcium with radiocalcium, three experiments were carried out in which gypsum was mixed for different lengths of time with the radioactive solution. The result is seen in Table 2.

The results may be interpreted in this way. The finely pulverized miner-

Quartz	0.1 meqv/100 gr	
opal	0.3	-
gypsum	104.2	-
calcite	56.6	-
dolomite	3.3	-
magnesite	0.6	-
siderite	0.3	-
apatite	3.8	-
albite	0.5	-
anortite	2.1	-

Table 1. Mineral powder (< 5 μ) treated for approx. 25 minutes in a radiocalcium solution. The figures denote how many milliequivalents radiocalcium per 100 grammes are adsorbed on the calcium free minerals, and how many meqv/100 gr. have been adsorbed on and been exchanged in the surface of the calcium bearing minerals.

Gypsum treated	1 min.	56.4 meqv/100 gr
-	6 -	76.1 -
-	12 -	85.8 -

Table 2. Pulverized gypsum (< 5 μ) treated for different lengths of time in a radiocalcium solution. The figures denote how many meqv/100 gr have been adsorbed on and been exchanged in the surface.

als have some unneutralized bonds on the surfaces which will give rise to adsorption, and the measured adsorptions on the calcium free minerals, quartz, opal, magnesite, siderite and albite, must be due to this. The calcium bearing minerals will have a slight adsorption for the same reason, but besides this an exchange of inactive with radioactive calcium ions will take place in a reversible process, in which the total exchange is dependent upon the solubility of the mineral, the specific surface and the time employed.

In determinations of the cation exchange capacity of clays by the tracer technique with Ca-45 as tracer, the results here described mean that the samples must be without any notable amounts of gypsum and calcite (and aragonite).

## DANSK RESUMÉ

Ved mineralogiske og tekniske undersøgelser af lersedimenter og lermineraller er bestemmelsen af deres katjon udbytningsevne meget ofte af stor betydning. Til dette bestemmelsesarbejde har forskningsleder, dr. phil. I. TH. ROSENQVIST, Norges Geotekniske Institutt, Oslo, udviklet en god og hurtig, kvantitativ metode, hvor bestemmelsen udføres ved hjælp af den radioaktive isotop kalcium-45.

Ved adsorptionsundersøgelser af forskellige danske lerer efter denne metode viste der sig at opstå visse vanskeligheder med prøver, der indeholdt gips, idet resultaterne for samme prøve kunne variere mellem 60 og 90 mekv/100 g.

Talrige danske lerer indeholder kalkspat, og en del indeholder gips (BØGGILD 1943). Både disse og andre ikke-lermineraller er påvist i lerfraktionen i danske lerer (CLAUSEN 1932, UNMACK 1944, 1947, 1949 og GRAFF-PETERSEN 1955). Elektronmikrografiet fig. 1 viser gipskrystaller (eller spaltestykker) med største kantlængde på  $0,5\mu$ , der er fundet i en prøve af lillebæltler. MACEWAN (1951) giver desuden en oversigt over ikke-lermineraller, som hyppigt påtræffes i lerbjergarters lerfraktion.

For at bestemme nogle af disse mineralers indflydelse på jonudbytningen (ved pH 6,5), blev rene mineralprøver pulveriseret ( $< 5\mu$ ), og mineralpulverne blev behandlet på samme måde som lerprøverne ved adsorptionsundersøgelserne.

Fremgangsmåden er indgående beskrevet af ROSENQVIST (1954 og 1955), og da samme fremgangsmåde er benyttet her, skal der blot henvises til ROSENQVIST's afhandlinger.

Hver prøve på 0,5 g mineralpulver blev kraftigt oprystet i en radiokalcium-opløsning (6 mekv i 6 ml). Prøven var opslemmet i opløsningen i ca. 25 minutter, hvorefter den blev centrifugeret og rensset. Resultaterne af de 10 undersøgte mineraler er givet i tabel 1.

Det ses, at de kalciumfri mineraler har adsorberet mindre end 1 mekv/100 g, hvorimod de kalciumholdige mineraler har »adsorberet« mængder varierende mellem 2,1 og 104,2 mekv/100 g. Af de kalciumholdige mineraler har gips og kalkspat optaget de største mængder.

Gips er noget opløselig i vand, og kalkspat er delvis opløselig i  $\text{CO}_2$ -holdigt vand. Da den radioaktive opløsning fremstilles ved at opløse  $\text{CaCO}_3$  i saltsyre, vil der samtidig blive opløst noget  $\text{CO}_2$  i vædsken, der derved bliver mere aggressiv overfor kalkspat end rent vand.

Da mineralernes opløselighed således synes at spille en rolle for udbytningen af inaktive med aktive kalciumjoner, blev der udført 3 bestemmelser, i hvilke gips var opslemmet i ulige lange tidsrum i den radioaktive opløsning. Resultaterne heraf er givet i tabel 2.

Resultaterne af undersøgelserne må tolkes således: De fint pulveriserede mineraler har en del unneutraliserede bindinger på overfladerne, der forårsager adsorption, og de målte adsorptioner på de kalciumfri mineraler kvarts, opal, magnesit, jernspat og albit må skyldes dette forhold. De kalciumholdige mineraler må have en adsorption af samme grund, men desuden må der ske en udskiftning af inaktive kalciumjoner i mineraloverfladen med aktive kalciumjoner fra opløsningen. Denne proces er reversibel, og den totale mængde udskiftede joner afhænger af mineralets opløselighed, den specifikke overflade og den anvendte tid.

Såfremt denne metode anvendes til bestemmelse af lerers adsorptionsevne, må prøverne være uden nævneværdigt indhold af gips og kalkspat (og aragonit).

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