

Desalting tests of mine waters, Recsk, Hungary

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SUMMARY

The study discusses the reasons which have necessitated the treatment of the mine waters.

The high hydrocarbonate content of the mine waters in the Recsk mine has caused excessive precipitation in the pump system to an extent where its safe operation was endangered.

To prevent this precipitation several methods have been developed in laboratory. These methods have been tested and evaluated according their efficiency, feasibility and applicability in laboratory and pilot-plant scale.

The aeration method has been proved to be the most efficient method to treat these mine waters.

INTRODUCTION

At Recsk (northeastern part of the Mátra Mts) large copper ore reserves were found at considerable depth. After the surface explorations have been completed, the underground developments were commenced by sinking two shafts and drifts on two levels. Increasing volumes of water have been produced from these developments. The water has very high dissolved salt content.

The chemistry of the water is intensely affected by the nature of rocks of the aquifer. Sodium-hydrocarbonate is predominant in the water coming from the sediments surrounding the intrusion, while sulphate is the dominant component in the waters stored within the intrusion. These two types of water are intermixed along the contact zone. Besides sodium, the Ca and Mg are the dominant cations (from the limestone and dolomite), the sulphate and chlorine are the dominant anions after the hydrocarbonate. The chemical composition of the water is illustrated in Fig. 1.

The increasing amount of water to be pumped up to the surface means greater and greater problems, since insoluble carbonate precipitates in the pipelines and pumps, owing to the gradual change in the Ca-CO₂ equilibrium conditions. These precipitations reduce the diametrical space in these equipments, lessen the efficiency of water pumping and may as well cause serious damage in the whole system.

A cross section of a pipe is shown on Fig. 2. This pipe was used as downward water line from the -700 m. b.s.l. level to the sump beneath the shaft. The inner diameter of the pipe was 150 mm. This has decreased to 42 mm after 120 days operation.

It was therefore essential to develop a method suitable to prevent precipitations in the pumping system. At first the chemical composition of these precipitations have been analysed:

CaCO ₃	96,5 %
MgCO ₃	2,8 %
insoluble in acid	0,7 %

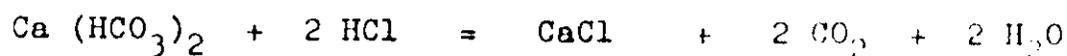
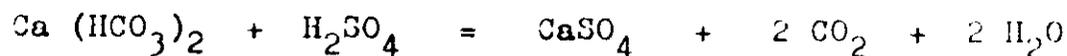
LABORATORY TESTS

The samples were taken from the -700 m. a.s.l. sump. These samples represent the quality of the pumped mine water. The samples were carried into the laboratory in sealed bottles. Each sample was analysed, and then treated.

Several methods were tested to treat the water:

1./ Acidization of hydrocarbonates

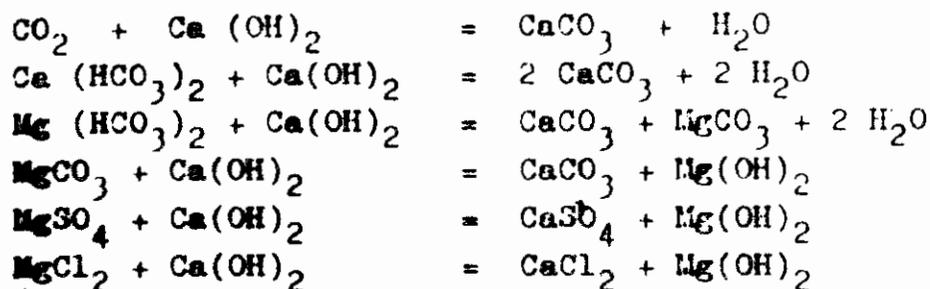
The mine water has 7,4-8,0 pH value. By adding strong acids (H₂SO₄, HCl) the dissolved hydrocarbonates dissociate, and carbon-dioxide is produced:



Thus the precipitation of carbonates is prevented. The main advantage of this method is that no precipitation is produced. It has to be used with great care, however, since the pH value should not shift into the acidic range, otherwise it may cause excessive corrosion. The strong acids may dissociate the floating carbonate particles, which is resulted in excessive acid consumption. The underground transport and handling of the sulphuric acid (or HCl) is troublesome, dangerous, and adversely affects the climatic conditions in the mine.

2./ The precipitation of carbonates with calcium-hydroxide-complete treatment

The following reactions take place:



The calcium-hydroxide is also used for melioration, the treat the NaHCO_3 content of soils.

The reactions illustrate that the whole carbonate content precipitates, and the Mg-hardness is replaced by Ca-hardness. Since the solubility of the $\text{Ca}(\text{OH})_2$ is low, the duration of the reactions is 4-5 hours.

This method is suitable to precipitate the carbonate from the mine water before it reaches the pumping system. The large amount of reagents required, and the large volume of precipitated salts are the disadvantages connected with this method.

3./ The precipitation of carbonates with reduced amount of $\text{Ca}(\text{OH})_2$

The encrustations, which have been analysed, consisted mainly of insoluble CaCO_3 . The rate of reaction and precipitation of the $\text{Ca}(\text{HCO}_3)_2$ is relatively large. Thus the amount of added $\text{Ca}(\text{OH})_2$ has been reduced in the further tests.

Three tests have been carried out with 20-20 l samples, which have had similar composition. The samples were treated by different amounts of calcium hydrate, and the water was periodically analysed.

The following tests have been made:

- (1) Addition of calcium-hydrate in quantities necessary for the precipitation of the dissolved CO_2 and Ca^{2+} content, as estimated from the chemical composition of the water.
- (2) Addition of calcium-hydrate in quantities necessary for the precipitation of the dissolved CO_2 , Ca^{2+} , Mg^{2+} content, and for the chemical alteration of the Mg-salts.
- (3) Addition of calcium-hydrate in quantities necessary to precipitate the dissolved CO_2 and the total HCO_3^- and for the chemical alteration of the Mg salts.

The changes in the HCO_3^- ; CO_3^{2-} ; Ca^{2+} ; and Mg^{2+} contents are shown in Figs 3-6.

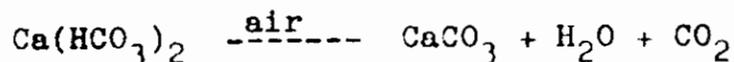
The percentage of the precipitated Ca^{2+} content has shown the following values

test No.	Ca^{2+} %	pH
1	79	7,9
2	91	8,4
3	93	9,2

As is shown from these figures, 24-50 % of the calcium hydrate required for a complete treatment can give good results, and provides more favourable pH values. (No. 1. and 2. tests)

4./ Aeration and complex treatment tests

During aeration dissolved CO_2 is removed from the water, the Ca-CO_2 equilibrium no longer exist, and those carbonates, which have low solubility, precipitate.



Tests were made with and without simultaneous calcium-hydrate treatment.

20 l samples were treated with aeration using 5 l/min flow rate for 14 hours. Four tests have been carried out, using samples, which have had same composition:

- (1) Aeration without calcium-hydrate treatment.
- (2) Aeration with calcium-hydrate treatment (in amount suitable to precipitate the dissolved CO_2 and Ca^{2+} content.)
- (3) Aeration with calcium-hydrate treatment (in amount suitable to precipitate the dissolved CO_2 , Ca^{2+} and Mg^{2+} content and to alter the Mg salts).
- (4) Calcium-hydrate treatment (in amount suitable to precipitate the dissolved CO_2 and the total HCO_3^- content and to alter the Mg salts) without aeration.

The results are shown on Figures 7, 8, 9, and 10.

The amount of the precipitated Ca^{2+} content compared to the total dissolved Ca^{2+} content has shown the following values after 4 hours aeration:

	Ca^{2+} %	pH
1.	92	8,9
2.	97	9,0
3.	98	9,2
4.	95	9,4

Thus it was revealed that the application of reduced amount of calcium hydrate (25 %) with simultaneous aeration has led to better results than the complete calcium-hydrate treatment.

5./ Aeration with different flow rates

In these tests different air flow rates were used. Three samples were tested. Aeration time was 4 hours. The results are as follows:

	Flow rate	Ca ²⁺ %	pH
1.	1 l/min	95	8,6
2.	5 l/min	96	8,7
3.	10 l/min	97	8,9

The dissolved Mg²⁺ content has not been affected by the aeration. The variations of the HCO₃⁻, CO₃²⁻ and Ca²⁺ contents are shown on Figs. 11-13.

The aeration has given very good results, but the minimum 2 hours aeration time could not be accepted in underground working conditions.

6./ Tests with intensified aeration

Based on the previous results, the aeration time had to be reduced by intensifying the process. A small flotation-cell was used, with 5 l/min air flow rate.

The aeration times were 1 min, 2 min, 3 min, 5 min, 10 min. After treatment the water was settled. Samples were taken and analysed after 10, 20, 30, 40, 50, 60, 90, 120, 150, 180, 210, 240 minutes. After 4 hours settling time, the precipitated amount of Ca²⁺ was as follows:

Aeration time min	Ca ²⁺ %	pH
1	11	7,6
2	32	7,6
3	35	7,65
5	41	7,65
10	50	7,65

7./ Intensified aeration with calcium-hydrate treatment

As the results of the short, intensified aeration tests were not encouraging, this method was combined with calcium-hydrate treatment. The aeration time was 3 min. The amounts of the added calcium-hydrate were 10, 20, 40 % of the amount required for a complete treatment. This has been added in dissolved form, with 2 % concentration into the flotation cell. The treated samples were settled for 4 hours, and then analysed.

The results after 4 hours settling time:

	the amount of Ca(OH)_2 used	Ca^{2+} %	pH
1.	0	35	7,65
2.	10	60	7,80
3.	20	70	8,00
4.	40	86	8,30

The calcium-hydrate treatment has reduced the Mg^{2+} content too.

8./ The effect of the air-water interface to the quality of the water:

The decomposition of hydrocarbonates depend not only from the quantity of air but also the size of the air-water interface. Samples with the same composition and quantity were poured into cylinders having different diameters. The samples were settled for 70 hours, and analysed in each hour. The change of the Ca^{2+} content is illustrated on Fig. 14., and the results obviously show the influence of the air-water interface in the carbonatisation process.

As a consequence, three main factors were considered to have major effect on the decomposition of hydrocarbonates:

- 1./ the aeration time
- 2./ the air-water interface
- 3./ the amount of added calcium-hydrate.

UNDERGROUND TESTS

The first underground test series has aimed to prove the efficiency of the process in routine working conditions.

The tests were carried out on the -700 b.s.l. level of the mine, at the 1001 sump drift. The arrangement is illustrated in Fig. 15. The mine water from the main-haylage drainage has flown into the A section of a small 3 m³ sampling sump. From here it was pumped into the mixer line which has consisted of two Denver flotation cells. The 1001 sump drift has been separated by dams into three sections. From the mixer the water discharged through pipes into the No 1. section of the sump-drift.

The water which has not been treated, has directly overflowed from the A to the B section of the small sampling sump. The air supply has been provided from the compressed air-line.

Two alternative aeration methods have been used:

- (1) through the mixing head of the flotation cell
- (2) through 60 mm perforated pipes in the No I and II sump sections.

The calcium-hydrate has been added manually in powder form into the flotation cell.

The water was sampled in the drainage before the mixer, after the mixer, at the dams of the No I. section, No. II. section and No. III section of the sump drift, and before the discharge into the B section of the sampling sump.

The samples were analysed on site, and the "p", "m", pH values, as well as the Ca^{2+} , Mg^{2+} and dissolved CO_2 contents were determined.

The air-flow rate has not been measured.

The following tests have been completed:

- 1./ 500 l/min water flow rate, small air flow through the mixing head of the flotation cell, 80 % calcium-hydrate (compared to the amount required for a complete treatment);
- 2./ 500 l/min water flow rate, small air flow through the mixing head of the flotation cell, 40 % calcium-hydrate;
- 3./ 500 l/min water flow rate, maximum air flow through the mixing head of the flotation cell, 20 % calcium-hydrate (compared to the amount required for complete alteration);
- 4./ 500 l/min water flow rate, maximum air flow through the mixing head of the flotation cell, 20 % calcium-hydrate (compared to the amount required for a complete treatment);
- 5./ 500 l/min water, maximum air flow through the mixing head of the flotation cell, without calcium-hydrate treatment;
- 6./ 1300 l/min water maximum air flow through the mixing head of the flotation cell, without calcium-hydrate treatment;
- 7./ 1300 l/min water, maximum air flow through the mixing head of the flotation cell, with 20 % calcium-hydrate (compared to the amount required for a complete treatment);
- 8./ 1300 l/min water, maximum air flow through the mixing head of the flotation cell, with 40 % calcium-hydrate (compared to the amount required for the complete alteration);

- 9./ 1300 l/min water, maximum air flow through perforated pipe, without calcium-hydrate treatment;
- 10./ 1300 l/min water, maximum air flow through perforated pipe, 20 % calcium-hydrate (compared to the amount required for the complete alteration).

The amount of precipitated Ca^{2+} has shown the following values:

test No.	Ca^{2+} %	pH	test No.	Ca^{2+} %	pH
1.	93,9	8,6	6.	64,1	7,5
2.	91,1	8,2	7.	78,8	7,8
3.	77,3	7,8	8.	92,7	8,1
4.	83,3	7,9	9.	83,0	7,6
5.	66,7	7,5	10.	88,7	7,9

The results have proved that even with the least favourable test conditions 64 % of the dissolved Ca^{2+} content can be precipitated from the mine water. This minimum value was obtained in the No. 6. test, where 1 min aeration time was used, without addition of calcium-hydrate. The analogous laboratory test has given 11 % Ca^{2+} value. The best results were obtained from the No. 1. test, though this has not been considered feasible owing to the excessive calcium-hydrate consumption and the large volume of precipitates.

The underground tests have proved that the majority of the Ca^{2+} -content can be precipitated by aeration and calcium-hydrate treatment before the water reaches the pumping system. It was necessary to determine the extent of water treatment required to protect the system. In order to do this, the mine water was regularly sampled in the mine-drainage system and on the surface during one month period. The analyses have shown that 40-60 % of the dissolved Ca^{2+} has been precipitated in the pumping system. This the water treating system was designed to precipitate 80 % of the dissolved Ca^{2+} content.

In the next tests the proper technical parameters were determined. The water flow rate, the air flow rate was measured, the quality of the water was analysed. The aeration was carried out in the sump, both perforated pipes were placed in the No. I. section of the sump. The water pumped out the surface was also analysed.

The duration of each test was one week. The results were as follows:

Test	Ca^{2+}	pH
1. 1300 l/min water, 5 m ³ /min air	77,6	7,35
2. 1300 l/min water, 2 m ³ /min air	62,8	7,35
3. 1300 l/min water, 3,5 m ³ /min air	69,3	7,50
4. 1300 l/min water, 5 m ³ /min air Ca(OH) ₂ in 10 % amount of total required to complete alteration	85,7	7,80
5. 1300 l/min water, 5 m ³ /min air, Ca(OH) ₂ in 20 % amount of total required to complete alteration	88,1	8,00

The difference between the Ca^{2+} contents of the treated water and the pumped water on the surface remained below 1 %, which meant that no carbonate has precipitated in the pump system.

When the tests have been completed, the aeration treatment has been proposed, with 3 m³ air/l m³ mine water rate. The results can be improved by the addition of Ca(OH)₂, though this improvement means excessive cost (material, transport, storage, treatment costs).

The water treatment process has been in operation for more than a half year. During this period no down-time was connected with precipitation in the system, which is the best evidence of the efficiency of the process.

List of figures

Fig. 1. Legend

- | | |
|---------------------|--------------------|
| 1. NaHCO_3 | 3. Mixed character |
| 2. CaSO_4 | 4. Drill-hole |

Fig. 2. A slice from the pipe-line between -700 m.Bf. and -900 level after 120 days operation.

Fig. 3. The variation of the hydrocarbonate content during the calcium-hydrate treatment

1. for the precipitation of the dissolved CO_2 and Ca^{2+} content
2. for the precipitation of the dissolved CO_2 and Ca^{2+} content and for the alteration of the Mg salts.

Fig. 4. The variation of the carbonate content during the calcium-hydrate treatment.
For legend see Fig. 3.

Fig. 5. The variation of the Ca content during the calcium-hydrate treatment.
For legend see Fig. 3.

Fig. 6. The variation of the Mg content during the calcium-hydrate treatment.
For legend see Fig. 3.

Fig. 7. The variation of the hydrocarbonate content during complex water treatment

1. 5 l/min air	0 g/20 l	mine water
2. 5 l/min air	12 g/20 l	mine water
3. 5 l/min air	25 g/20 l	mine water
4. 0 l/min air	48 g/20 l	mine water

Fig. 8. The variation of the carbonate content during complex water treatment.
For legend see Fig. 7.

Fig. 9. The variation of the calcium content during complex water treatment.
For legend see Fig. 7.

Fig. 10. The variation of the magnesium content during complex water treatment.
For legend see Fig. 7.

Fig. 11. The variation of the hydrocarbonate content with different rates of aeration

1. 1 l/min air,	20 l	mine water
2. 5 l/min air,	20 l	mine water
3. 10 l/min air,	20 l	mine water

Fig. 12. The variation of the carbonate content with different rates of aeration.
For legend see Fig. 11.

Fig. 13. The variation of the calcium content, at intense aeration and addition different amounts of calcium-hydrate.

1. 10 % calcium-hydrate of the amount required for complete treatment
2. 20 % calcium-hydrate of the amount required for complete treatment
3. 40 % calcium-hydrate of the amount required for complete treatment.

Fig. 14. The variation in the Ca^{2+} content of the mine-water with the size of air-water interface

1. d = 80 mm
2. d = 125 mm
3. d = 230 mm
4. d = 360 mm.

Fig. 15. The schematic diagram of the underground mine-water treatment system.

Legend: ----- compressed air
-.-.-.- water

Fig. 16. The variation of the concentrations of the eight main components of water during treatment

Legend: _____ before treatment
----- after treatment

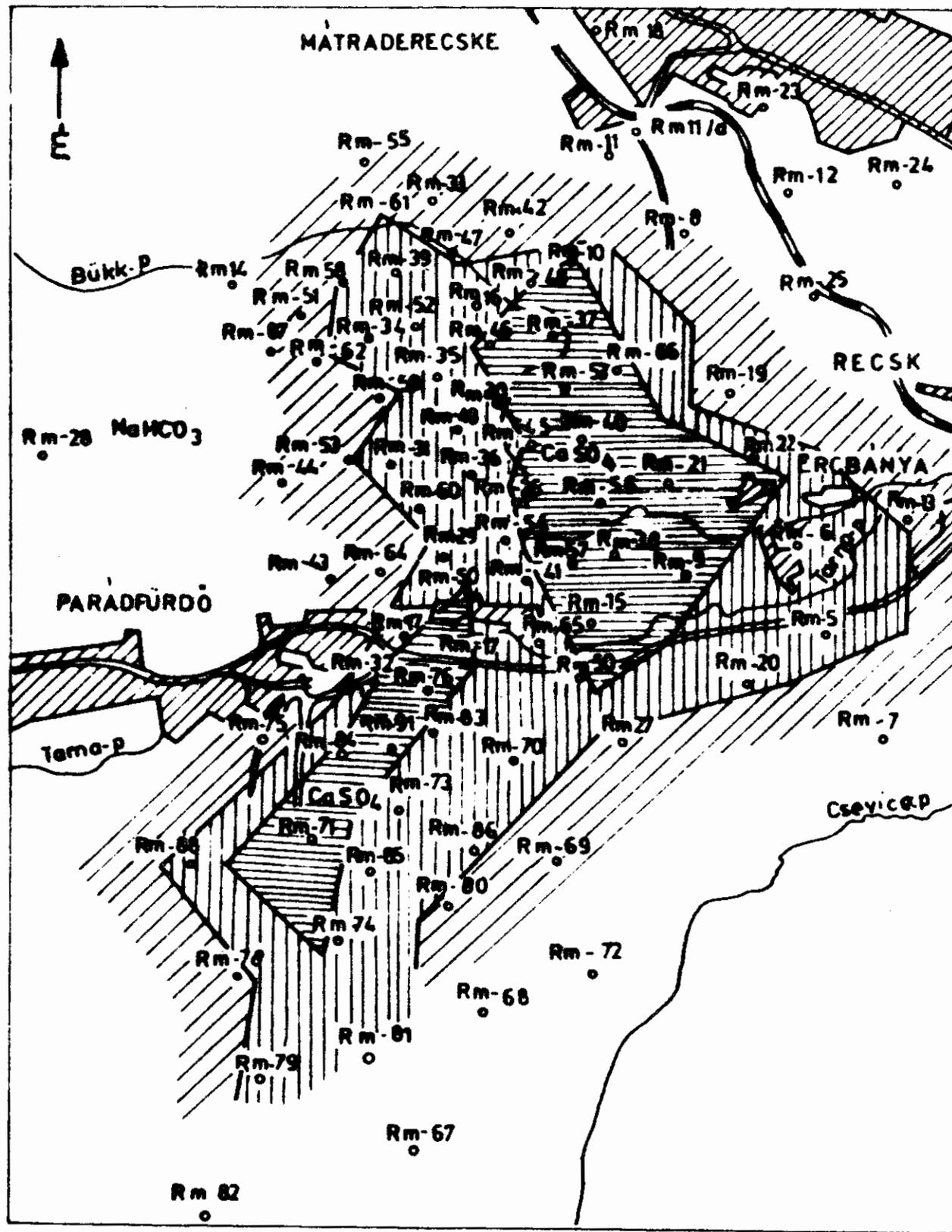


Fig. 1sz ábra.

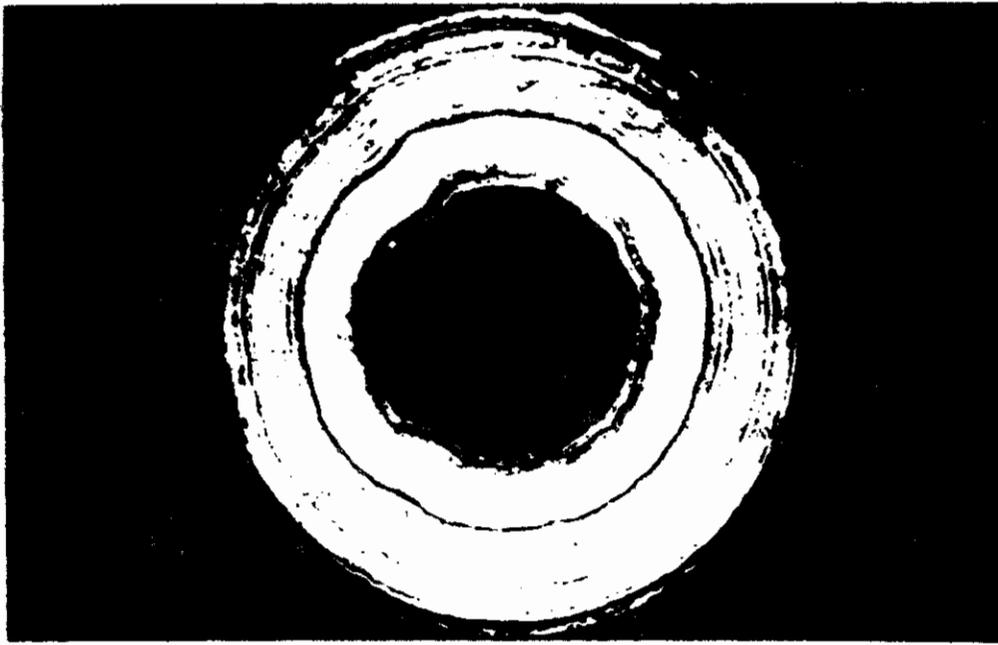


Fig. 2. abra

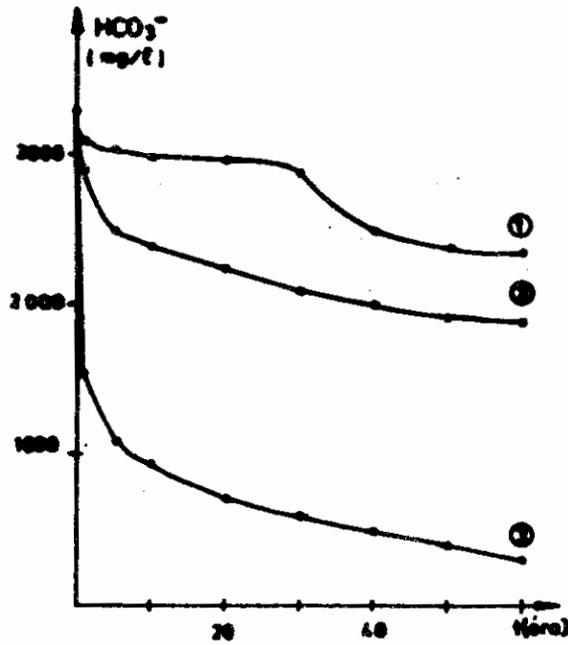


Fig. 3.sz ábra

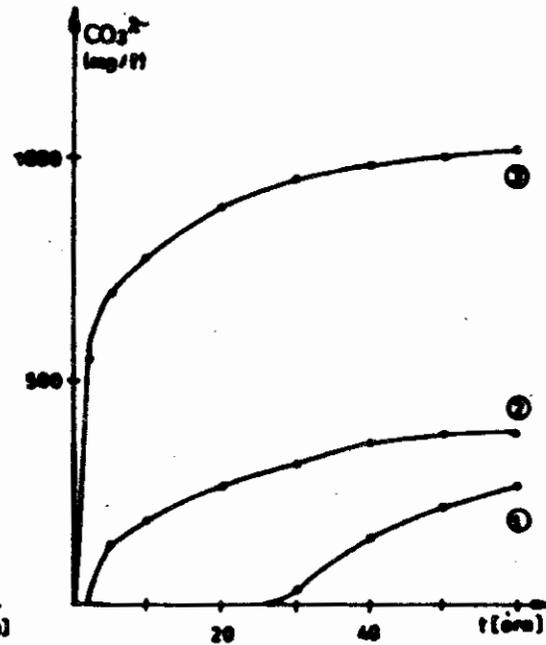


Fig. 4.sz ábra

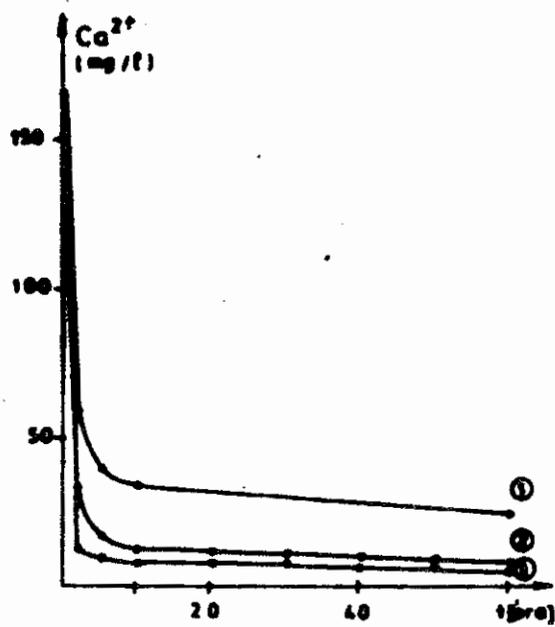


Fig. 5.sz ábra

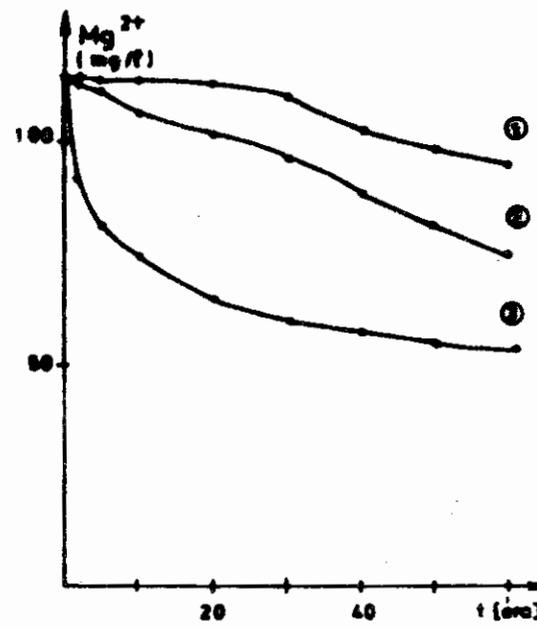


Fig. 6.sz ábra

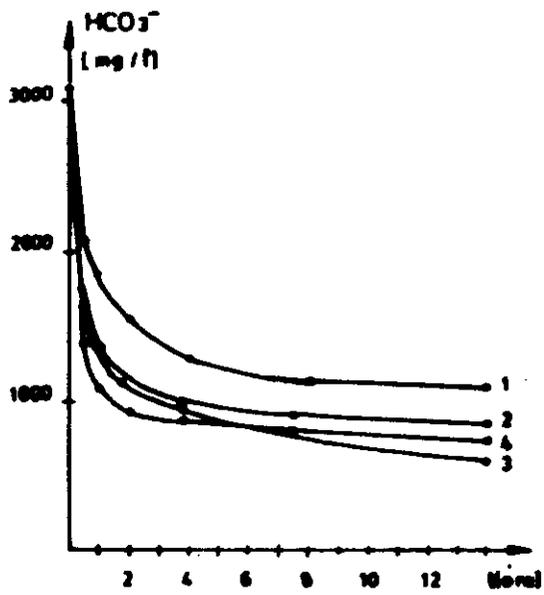


Fig. 7.sz ábra

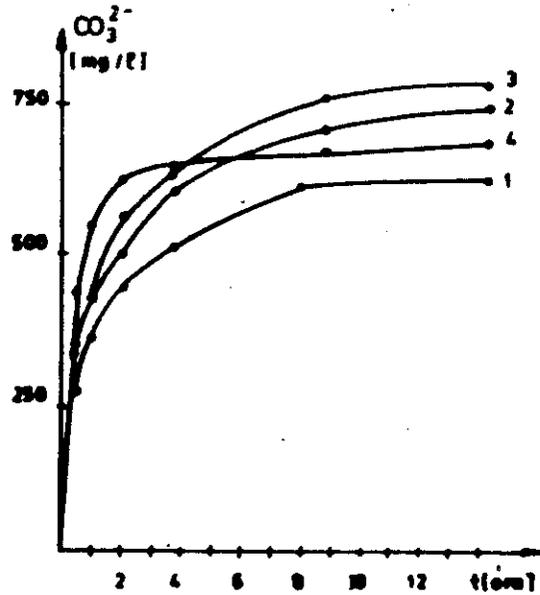


Fig. 8.sz ábra

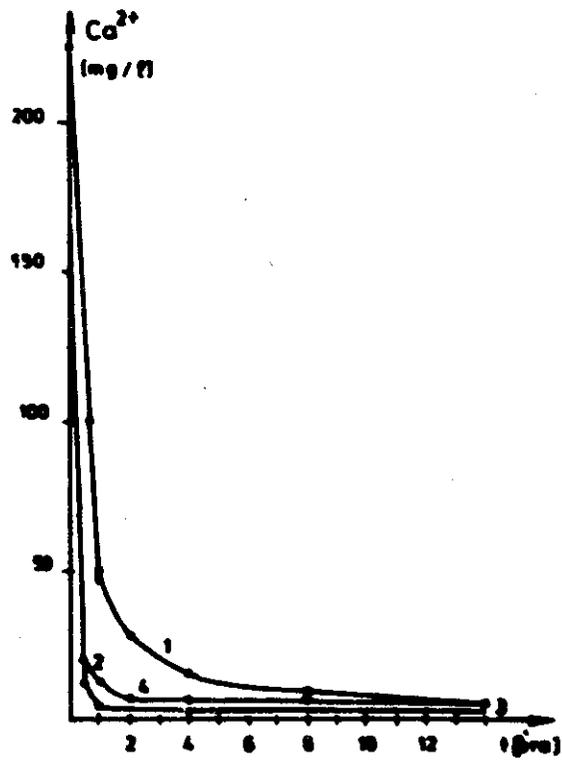


Fig. 9.sz ábra

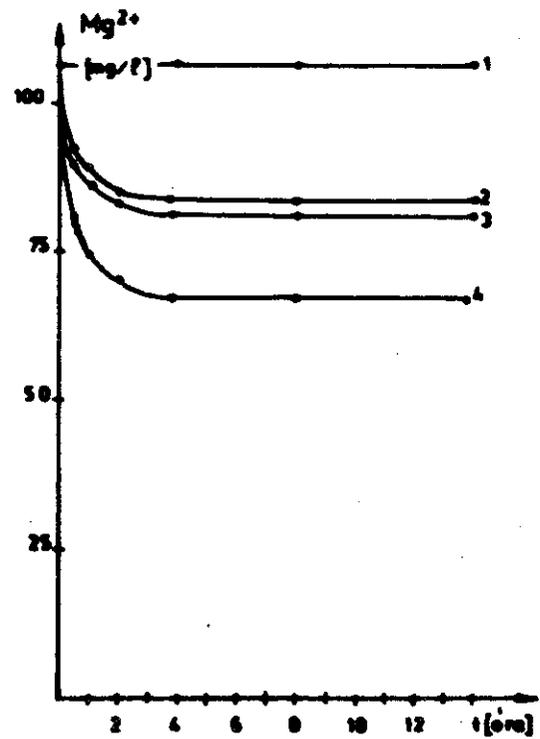


Fig. 10.sz ábra

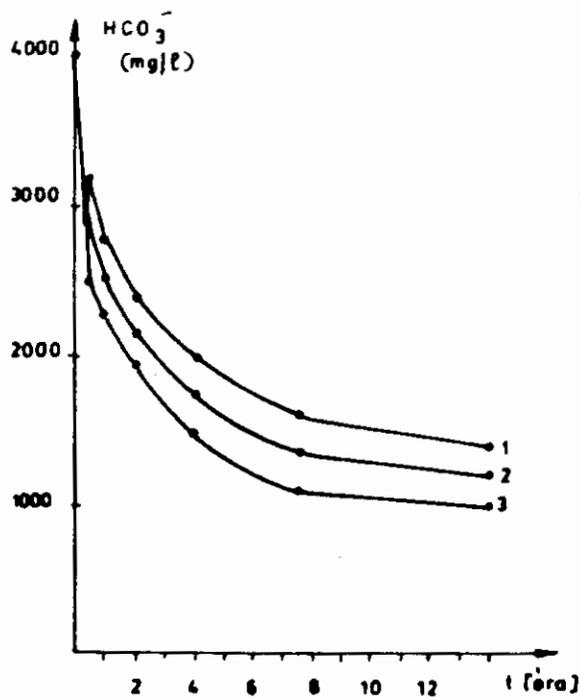


Fig. 11. sz ábra

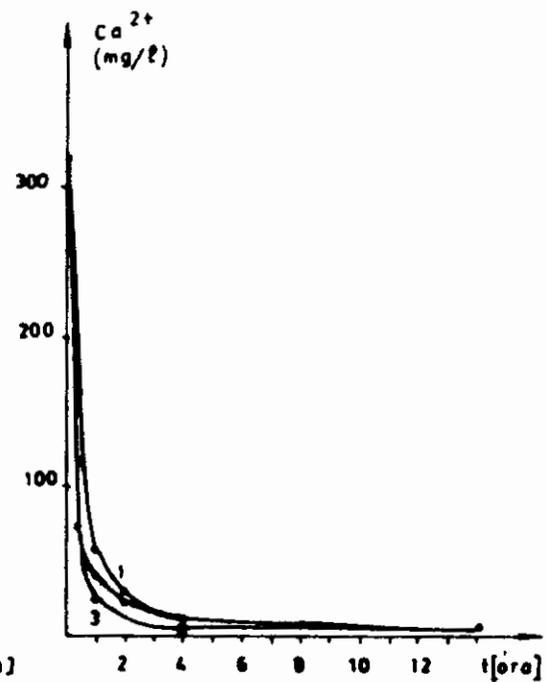


Fig. 12. sz ábra.

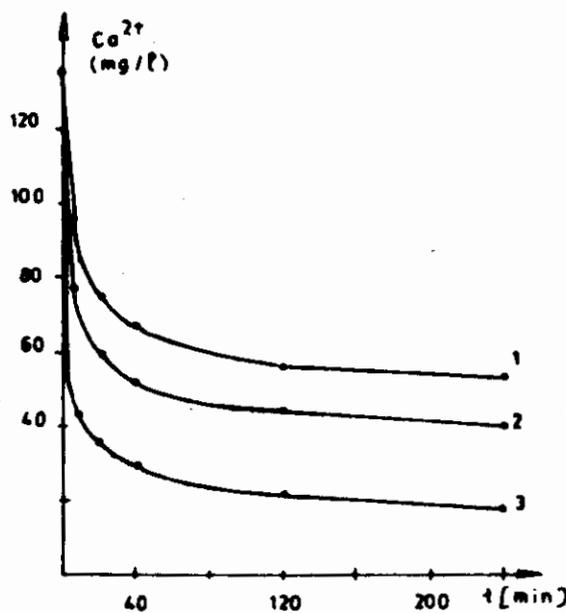


Fig. 13. sz ábra

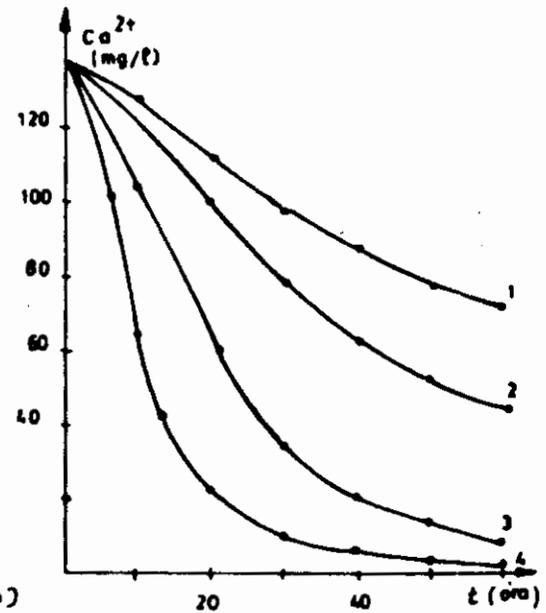


Fig. 14. sz ábra.

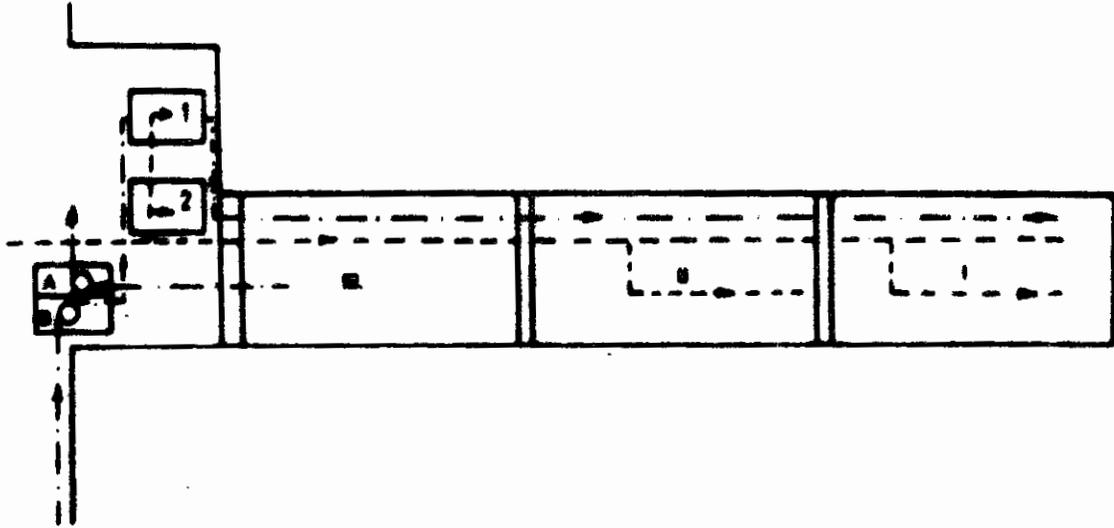


Fig. 15 ábra.

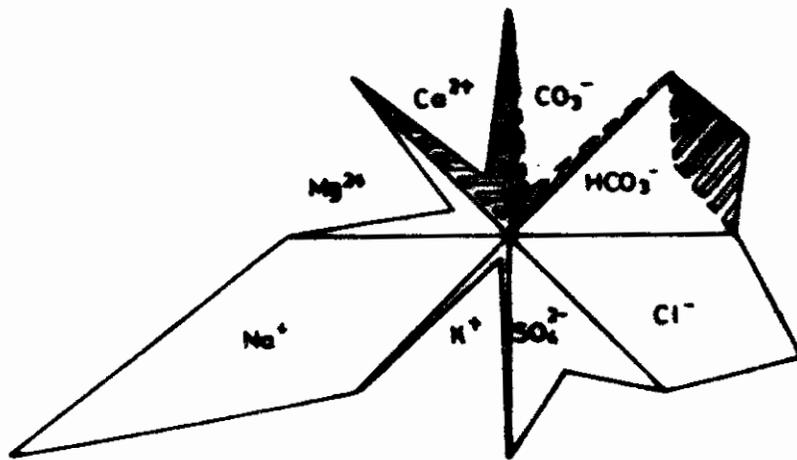


Fig. 16 ábra.